

SECOND EDITION

Engineering Chemistry

Fundamentals and Applications

Shikha Agarwal



CAMBRIDGE

Engineering Chemistry

Engineering chemistry discusses fundamental theoretical concepts of chemistry and links them with their engineering applications. First and second semester engineering students in various technical universities study the subject, and this textbook has been designed to meet their course requirements in a comprehensive manner. It supplements its treatment of the fundamental concepts and their applications by scores of illustrations and learning exercises. Lucid language and an easy-to-learn approach will enable the readers to assimilate the basic concepts and also facilitate comprehension by students not so strong in English language skills. This revised, second, edition builds on the success and popularity of the first 2015 edition, which was adopted as a text/reference book by several universities.

In addition to the topics in the first edition, this edition deals with new topics such as a detailed discussion of renewable energy sources, nuclear fuels, defluoridation of water by Nalgonda technique and domestic waste water management, periodic properties including classification of elements, periodicity in properties and types of elements on the basis of their electronic configuration, periodic trends in properties like atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, Fajan's rule and oxidation states of elements of various groups, different theories of acids and bases like the Arrhenius theory, Bronsted–Lowry concept, solvent system definition of acids and bases, Lewis concept, hard–soft acids and bases, oxidation and reduction with its applications to the extraction of metals, Ellingham diagram, molecular interactions, real gases and critical phenomenon, topics on quantum chemistry such as Schrodinger wave equation, particle in a one- and three-dimensional box, Schrodinger wave equation for hydrogen and hydrogen-like system, Huckel molecular orbital theory for conjugated system, semiconductors, superconductors and magnetic materials, potential energy of surfaces, trajectories on potential energy surfaces, thermodynamic formulation of the transition state theory, topics related to molecular spectroscopy like the Franck–Condon principle, rotational (microwave) spectroscopy of diatomic molecules, vibrational rotational spectra of diatomic molecules, Raman spectroscopy and applications of NMR spectroscopy in magnetic resonance imaging, drugs, absolute configuration of organic compounds, coordination chemistry, nomenclature of coordination compounds, bonding and isomerism in coordination compounds. The chapter on basics of environment science has been removed in this edition.

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CAMBRIDGE
UNIVERSITY PRESS

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University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, vic 3207, Australia

314 to 321, 3rd Floor, Plot No.3, Splendor Forum, Jasola District Centre, New Delhi 110025, India

79 Anson Road, #06-04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning and research at the highest international levels of excellence.

www.cambridge.org

Information on this title: www.cambridge.org/9781108724449

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First published 2015

Second edition 2019

Printed in India

A catalogue record for this publication is available from the British Library

ISBN 978-1-108-72444-9 Paperback

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To
His Holiness Shri Shivkripanand Swami

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Preface to Second Edition

The wide popularity and acceptance of the first edition was the main motivation behind the second edition. The first edition found its place as a text/reference book in the syllabus of several universities. Several improvements have been made in this edition; the obscurities in the earlier edition have been removed and several new topics have been added as per the AICTE model curriculum.

In *Chapter 1*, 'Fuels', the portion on renewable energy sources, which was just touched upon in the first edition, has been elaborately written; a descriptive study of nuclear fuels has been added along with chemical fuels. *Chapter 2*, 'Water', includes many new topics such as break point chlorination, defluoridation of water by Nalgonda technique and domestic waste water management. *Chapter 3*, 'Corrosion', has been revised. Several figures have been replaced and a myriad of examples on different types of corrosion both from day-to-day life and from industry have been introduced. *Chapter 4*, 'Phase Rule', the iron-carbon alloy system has been rewritten. *Chapter 8*, 'Periodic Properties', and *Chapter 9*, 'Acid-Base, Oxidation-Reduction and Intermolecular Forces', are new to this edition. *Chapter 8* deals with the basic concepts of classification of elements, periodicity in properties, types of elements on the basis of their electronic configuration, periodic trends in properties like atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, Fajan's rule and oxidation states of elements of various groups; *Chapter 9* discusses the different theories of acids and bases such as the Arrhenius theory, Bronsted-Lowry concept, solvent system definition of acids and bases, Lewis concept, hard-soft acids and bases, oxidation and reduction with its applications to the extraction of metals, Ellingham diagram, molecular interactions, real gases and critical phenomenon. *Chapter 10*, 'Atomic Structure and Chemical Bonding', covers new topics like Schrodinger wave equation, particle in a one- and three-dimensional box, Schrodinger wave equation for hydrogen and hydrogen like system, Huckel molecular orbital theory for conjugated system. *Chapter 11*, 'Solid State', has been augmented with the theory of semiconductors, superconductors and magnetic materials. Potential energy of surfaces, trajectories on potential energy surfaces and thermodynamic formulation of the transition state theory have been included in *Chapter 13*, 'Chemical Kinetics'. In *Chapter 15*, 'Thermodynamics', and *Chapter 16*, 'Electrochemistry', several sign conventions have been changed in accordance with the latest IUPAC conventions. Several portions of these chapters have been rewritten to facilitate understanding. Several new topics have been added to *Chapter 17*, 'Spectroscopy'; topics related to molecular spectroscopy missing in the earlier edition have been included. The new topics included are Franck-Condon principle, rotational (microwave) spectroscopy of diatomic molecules, vibrational rotational spectra of diatomic molecules. Raman spectroscopy and applications of NMR spectroscopy in magnetic resonance imaging has also been discussed. IR spectra of several compounds given in the first edition have been removed and the important absorption peaks have been tabulated.

Drugs and absolute configuration of organic compounds has been included in *Chapter 19*, 'Fundamentals of Organic Chemistry'. *Chapter 20*, 'Coordination Chemistry', with topics like nomenclature, bonding and isomerism in coordination compounds, is again a new chapter in this edition. To contain the size of the book *Chapter 21*, 'Basics of Environment Science', has been removed from this edition.

Illustrations, new figures, numerical problems and scores of new examples have been included. I hope with all these changes, the book will meet the expectations of the students and teaching fraternity across the country. Although great care has been taken to make the book as error free as possible, yet 'to err is human and to forgive is divine'. I extend apologies for the errors left inadvertently and look forward to the cooperation of the faculty and students in bringing these errors to my notice so that they can be rectified in future.

Preface to First Edition

Engineering chemistry is taught as a compulsory subject to first year undergraduate students of all the branches of engineering. The scope of the subject is very wide and writing a book for such a heterogeneous variety of students across the country was a challenging assignment. The needs of the students are diversified and incorporate a combination of both traditional topics and the latest trends in the subject including emerging areas like liquid crystals, green chemistry and nanochemistry.

This book has been organised to meet syllabi requirements of almost all Indian universities. The aim of this text is to enable the student to develop capabilities in self learning and understanding. It is a student oriented book and my teaching experience, stretching more than two decades, gave me insight into the mental status of the students at this level and the problems they confront while studying the subject. Two important facts have been kept in mind one, students reading this text are taking their first steps into the world of technical education and two, that English is a second language for most of these students.

Keeping these objectives in mind the book has been written in very simple language. The book has nearly 350 figures and illustrations, over 500 solved, unsolved problems along with review questions and it also includes more than 450 multiple choice questions.

All chapters are provided with highly descriptive and well labeled figures. A simple look at a figure will enable the student to grasp the underlying description. Theoretical explanations have been supplemented with solved and unsolved problems wherever required to enhance the process of understanding, learning and reproducing the principles involved. The problems have been blended with the text so that the student need not turn pages. The book aims to familiarize the student with the university pattern of examination: to meet this objective, numerical problems that have appeared in various university and board exams have been included at appropriate places.

Organisation of the book

The book has been organised into twenty four chapters. It begins with topics of common interest like fuels, water, corrosion and phase rule followed by engineering materials, polymers and lubricants. The book then incorporates fundamental topics: structure and bonding, solid state, liquid crystals, chemical kinetics, surface chemistry, thermodynamics, electrochemistry, spectroscopy, photochemistry, fundamentals of organic chemistry, organometallic chemistry, green chemistry, nanochemistry, basics of environmental chemistry, chemical aspects of biotechnology, analytical techniques in chemistry, chemistry of compounds of carbon and hydrogen.

Chapter one, Fuels, introduces the student to the basic definition of fuels, then proceeds to describe different types of fuels, their occurrence, purification, composition and uses. In addition it discusses the

manufacture of fuels. The chapter also outlines renewable energy sources and their utility in the present scenario. *Chapter two* on water lays emphasis on the industrial end uses of water with special emphasis on hard water and its effects in industry. It deals with the principles involved in the softening of water like zeolite method, ion exchange method and it explains the latest techniques for desalination of brackish water by reverse osmosis and flash evaporation process. The chapter devotes a section to the analysis of hard water. Corrosion has a massive impact in industry and its study is of great significance for an engineering student. *Chapter three* underlines the causes, effects and measures to control corrosion. The latter half of this chapter lays special emphasis on corrosion control and outlines techniques like galvanising, tinning, hot spraying, electroplating, electroless plating, organic coatings, etc. Similarly phase rule, engineering materials (cement, glass, refractories, abrasives and insulators), polymers are very important topics for the students at this level. These topics have been covered in *chapters four, five and six* respectively. The chapter on phase rule familiarizes the student with the fundamentals like what is a phase, what is a component, what are degrees of freedom, what is a phase diagram, difference between a true equilibrium and a metastable equilibrium and other fundamentals. To clarify these basic concepts, definitions are followed-up by plenty of examples. After ensuring that the student has grasped the basics, the chapter proceeds to explain the phase diagrams of various one component and two component systems and their applications. The second half of the chapter deals with metals and their alloys. This topic is important for understanding the behaviour of metals, their properties and variations in their properties depending on different phases and their composition. It explains advantages of alloys over pure metals and also explains the properties and uses of common alloys.

Chapter six on polymers not only explains fundamental concepts and basic definitions but also deals with the properties like glass transition temperature, viscoelasticity, anelasticity which are of immense industrial utility. The chapter explains various polymerisation techniques like bulk polymerisation, solution polymerisation and suspension polymerisation. Plastics and their manufacturing techniques like compression moulding, transfer moulding, blow moulding and extrusion moulding have been illustrated. Fibres and adhesives are also discussed. Apart from dealing with the preparation and uses of commonly known polymers the chapter lays special emphasis on speciality polymers like engineering thermoplastics, conducting polymers, electroluminescent polymers, liquid crystalline polymers like kevlar, biodegradable polymers and composite polymers like reinforced plastics.

Chapter seven on lubricants explains the significance, properties and types of lubricants; their selection and suitability for different types of machinery. *Chapter eight* on structure and bonding deals with the fundamental principles and various theories of bonding in molecules like valence bond theory, molecular orbital theory, band theory of solids. The chapter explains basic concepts like hybridisation, overlap of orbitals, filling of electrons in the orbitals and also explains the dual nature of matter, de-Broglie relationship and Schrodinger wave equation. *Chapter nine* highlights the fundamentals of solid state. It explains fundamental concepts like unit cell, crystal lattice, packing of crystals, Braggs law and the structure of common crystals. To help the student visualize these structures, the chapter has plenty of figures. Moreover numerical problems to enhance understanding of crystals have been integrated into the text. *Chapter ten* gives an introductory idea about the fourth phase of matter – liquid crystals.

Chapters eleven, twelve, thirteen, fourteen and sixteen cover important topics in physical chemistry like chemical kinetics, surface chemistry, thermodynamics and photochemistry. Special care has been taken to illustrate the derivations step by step. Important relations and mathematical formulae have been provided in the summary of these topics. I am hopeful that the formulae given at the end will be very useful for students and instructors in understanding the basic concepts and theory of these topics.

Chapter fifteen deals with ultraviolet, infrared and NMR spectroscopy. It explains the fundamentals, basic instrumentation required for spectroscopy study in different regions and the application of spectroscopic techniques in chemistry.

Chapters seventeen concerns itself with topics on organic chemistry. Fundamental organic concepts like inductive effect, resonance, hyperconjugation, electromeric effect, reaction intermediates like carbocation, carbanions, free radicals, nitrenes, carbenes have been discussed in sufficient details with lots of supporting examples. The chapter also discusses different types of organic reactions like addition, elimination, substitution and rearrangement reactions. Common name reactions alongwith their mechanism and applications have also been explained. Stereochemistry and its basic concepts have also been dealt. Organometallic compounds and their applications have been discussed in *chapter eighteen*.

To promote the concept of sustainable development green chemistry is gaining importance. The twelve principles of green chemistry and its applications are explained in *chapter nineteen*. *Chapter twenty* deals with nanochemistry. It gives an introductory idea to fundamentals like Top-Down and Bottom-Up approaches to nanoparticles. Important nanomaterials like carbon nanotube, nanowires, nanocones and haeckalites have been discussed in brief along with their applications. Fundamentals of environment science, pollution control, solid waste management and major environmental issues like acid rain, ozone depletion, wetland depletion, deforestation, biodiversity, soil erosion have been explained in sufficient detail in *chapter twenty-one*. Biotechnology is the application of technology to living organisms to modify products or processes for specific use. An introduction to the basic principles and their applications has been dealt with in *chapter twenty-two*.

The use of highly sophisticated instruments in science has made analysis accurate. *Chapter twenty-three* introduces the student to various analytical techniques in chemistry. The text ends with a discussion on the chemistry of carbon and hydrogen in the *last chapter*.

Throughout the text I have tried to maintain simplicity of language. Unnecessary details have been omitted and the book contains only as much material as is required for the target students. I hope it will serve its purpose and both teachers and students in various streams will benefit. I look forward to suggestions from esteemed faculty members and students, as their inputs will invariably help me to improve the book in future. Although great care has been taken to make the book as error free as possible but *to err is human*; I extend apologies for errors left inadvertently in the text and also look forward to suggestions from my friends and colleagues from the teaching fraternity across the country.

Acknowledgements

“To speak gratitude is courteous and pleasant, to enact gratitude is generous and noble, but to live gratitude is to touch heaven.”

A project of this dimension could not be completed without the support, advice and suggestions of colleagues, friends and family members. It is my divine duty to acknowledge the contribution of every person whose effort has made this project see the light of the day. I bow my head in reverence to my spiritual Guru and the almighty God for giving me the internal strength and self-discipline for this assignment. It is a well known fact that praise makes us complacent whereas criticism helps us to review our weaknesses and gives us an opportunity to improve. I am highly indebted to my first reviewer whose extremely critical review made me step out of my comfort zone and work to remove all types of obscurities in the book.

I extend sincere thanks to Professor C. P. Sharma (Retired Professor, MNIT, Jaipur), Dr Dinesh Gupta (Member Secretary, RPSC), Dr R. K. Upadhyay (Associate Professor and Head, Department of Chemistry, SPC Government College, Ajmer) for their suggestions and scholarly advice. I owe sincere gratitude to Dr Ranjan Maheshwari (Principal, Government Engineering College, Ajmer) for providing a positive work environment. I owe thanks to Dr Alok Khatri and Dr Amit Kumar Srivastava for going through certain portions of this book and giving me valuable inputs for improvement. I am also grateful to colleagues in my department Dr Sangeeta Krishnan, Dr Pooja Tomar and Dr Suresh Sahu for their valuable suggestions.

My family deserves a special mention. My husband Harsh Gupta stood behind me as a pillar of strength. My elder daughter Surabhi, a final year student of Computer Science branch at IIT Guwahati opened a plethora of web resources which were of great help in improving the content of the text. My younger daughter Kanishka studying in class eight deserves a special mention and acknowledgement as her golden time to be spent with me was sacrificed at the altar of this work.

In the end, I express my gratitude to the editorial team at Cambridge University Press; Gauravjeet Singh Reen (Commissioning Editor) for his excellent ground work and syllabus research that helped me in deciding the table of contents. I always turned to him for suggestions wherever I was stuck and he was always available to answer my queries. The editorial team did great work in editing the book trying to maintain uniformity in fonts and also editing grammatical errors throughout the book. I am extremely thankful and indebted to the marketing team at Cambridge who left no stone unturned to make this book reach out to the target group.

Last but not the least, I am thankful to all my students and teachers who have taught me and made me what I am today.

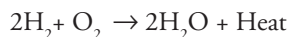
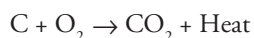
Chapter 1

FUELS

1.1 Introduction

A fuel is a substance that produces useful energy either through combustion or through nuclear reaction. An important property of a fuel is that the energy is released in a controlled manner and can be harnessed economically for domestic and industrial purposes. Wood, coal, charcoal, petrol, diesel, kerosene, producer gas and oil gas are some of the common examples of fuels.

Fuels that produce heat energy by combustion are termed as *chemical fuels*. During combustion, carbon, hydrogen, sulphur and phosphorus that are present in the fuel combine with oxygen and release energy.



However, combustion is not always necessary for a fuel to produce heat. Energy can also be liberated by fission or fusion of nuclei. This energy is much greater than the energy released by chemical fuels, and such fuels are termed as *nuclear fuels*. For example, plutonium, tritium, uranium, etc.

1.2 Classification of Fuels

Fuels can be classified on the basis of their (I) occurrence (II) physical state

(I) On the basis of occurrence, fuels are of two types

- (a) **Primary Fuels or Natural Fuels** These are found to occur in nature and are used as such either without processing or after being processed to a certain extent, which does

not alter the chemical constitution of the fuel. These are also known as fossil fuels. Examples include wood, peat, lignite, coal, petroleum, natural gas, etc.

- (b) **Secondary Fuels or Derived Fuels** These are the fuels that are derived from primary fuels by further chemical processing, for example, coke, charcoal, kerosene, producer gas, water gas, etc.

(II) On the basis of their physical state, fuels may be classified as follows:

- (a) Solid fuels
- (b) Liquid fuels
- (c) Gaseous fuels

The classification can be summarised as shown in the following diagram.

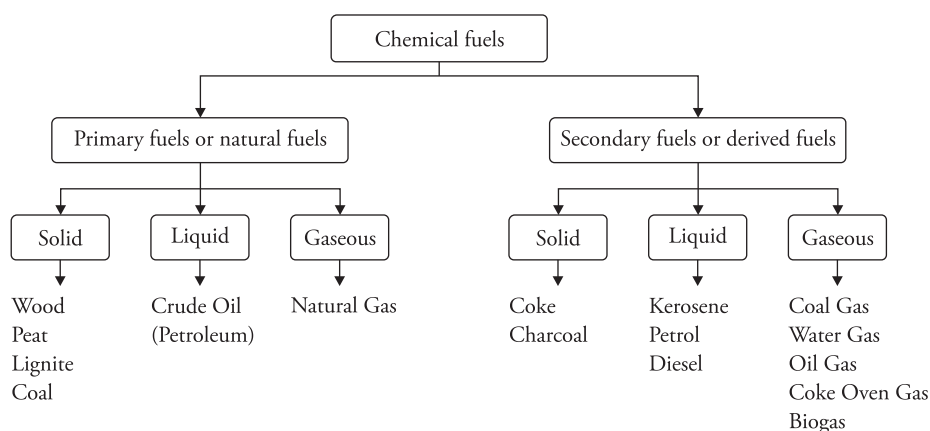


Figure 1.1 Classification of fuel

1.3 Characteristics of a Good Fuel

1. **High Calorific Value** A good fuel should possess high calorific value because calorific value determines the efficiency of the fuel. Higher the calorific value, greater is the heat liberated per unit mass or volume.
2. **Ignition Temperature** It is the lowest temperature to which a fuel must be preheated so that it starts burning smoothly. An ideal fuel should have moderate ignition temperature. Low ignition temperature can cause fire hazards, making storage and transportation difficult. Fuel with low ignition temperature can burn spontaneously leading to explosion. High ignition temperature, on the other hand, makes it difficult to kindle (ignite) the fuel.
3. **Moisture Content** Moisture content should be low because the presence of moisture lowers the calorific value of the fuel.

4. **Non-combustible Matter** After combustion, the non-combustible matter is left behind as ash or clinkers. Non-combustible matter reduces the calorific value of the fuel and also requires additional money investment for storage, handling and disposal of the waste products produced.
5. **Velocity of Combustion** If the velocity of combustion is low, then a part of the liberated heat may get radiated instead of raising the temperature; hence, the required high temperature may not be attained. On the other hand, if the velocity of combustion is very high then the rate of combustion might become uncontrollable. For a continuous supply of heat, fuel must burn with a moderate rate.
6. **Combustion Products** The products obtained during combustion of the fuel should be harmless and non-polluting. Harmful gases such as CO_2 , SO_2 , H_2S , PH_3 and PbBr_2 should not be produced, and also the amount of smoke produced should be less.
7. **Cost of the Fuel** A good fuel should be readily available at a low cost.
8. **Storage and Transportation** A good fuel should be easy to handle, store and transport at low cost.
9. **Size** In case of solid fuels, the size should be uniform so that combustion is regular.
10. **Combustion Should Be Controllable** The combustion process should be controllable, that is it can be started or stopped when required.

Table 1.1 Comparison of solid, liquid and gaseous fuel

S.No.	Solid Fuel	Liquid Fuel	Gaseous Fuel
1	Cheap and easily available	Costlier than solid fuel except in the countries of origin	Costly, because except natural gas all other gaseous fuels are derived from solid and liquid fuels
2	Convenient to store without any risk of spontaneous explosion	Great care must to be taken to store them in closed containers	Very large storage tanks are needed. Storing gaseous fuel requires extra care as they are highly inflammable
3	Large space is required	Storage space is less compared with solid and gaseous fuels	They must be stored in leak proof containers
4	They are easy to transport	They can be easily transported through pipelines	They can also be transported through pipelines
5	They possess moderate ignition temperature. Combustion is slow but it cannot be controlled easily	Combustion takes place readily and can easily be controlled or stopped by reducing or stopping the fuel supply	Combustion is fast and can be controlled and stopped easily
6	Ash is produced and its disposal is a big problem. Smoke is also produced	Ash is not produced, however fuels with high carbon and aromatic contents may produce smoke	Neither ash nor smoke is produced
7	They cannot be used in internal combustion engine	Used in internal combustion engine (petrol, diesel)	Used in internal combustion engines (CNG, LPG)

8	They have low thermal efficiency	Their thermal efficiency is higher than solid fuels	Their thermal efficiency is the highest
9	Their calorific value is lowest	Their calorific value is higher than solid fuels	Their calorific value is the highest
10	Least risk of fire hazards	Risk of fire hazards is high	Highest risk of fire hazards

1.4 Calorific Value

It is defined as the total amount of heat liberated when a unit mass or volume of fuel is burnt completely.

Units of heat

- (i) **Calorie** It is defined as the amount of heat required to raise the temperature of 1 g of water by 1 °C (from 15 °C to 16 °C)
 $1 \text{ calorie} = 4.185 \text{ Joules} = 4.185 \times 10^7 \text{ ergs.}$
- (ii) **Kilocalorie** It is defined as the amount of heat required to raise the temperature of 1 kg of water by 1 °C (from 15 °C to 16 °C). $1 \text{ kcal} = 1000 \text{ cal.}$
- (iii) **British Thermal Unit (BTU)** It is defined as the amount of heat required to raise the temperature of 1 pound (lb) of water by 1 °F (from 60 °F to 61 °F)
 $1 \text{ BTU} = 252 \text{ cal} = 0.252 \text{ kcal} = 1054.6 \text{ Joule} = 1054.6 \times 10^7 \text{ ergs.}$
- (iv) **Centigrade Heat Unit (CHU)** It is defined as the amount of heat required to raise the temperature of one pound of water by 1 °C (from 15 °C to 16 °C).
 $1 \text{ kcal} = 3.968 \text{ BTU} = 2.2 \text{ CHU}$

Units of calorific value

The units of calorific value for solid, liquid and gaseous fuels are given below.

System	Solid / Liquid fuels	Gaseous fuels
CGS	calories/g	calories/cm ³
MKS	kcal/kg	kcal/m ³
BTU	BTU/lb	BTU/ft ³

These units can be interconverted as follows

$$1 \text{ cal/g} = 1 \text{ kcal/kg} = 1.8 \text{ BTU/lb}$$

$$1 \text{ kcal} = 0.1077 \text{ BTU/ft}^3$$

$$1 \text{ BTU/ft}^3 = 9.3 \text{ kcal/m}^3$$

Gross and Net Calorific Value

Gross Calorific Value (GCV) It is also called higher calorific value (HCV) and is defined as the total amount of heat produced when a unit quantity (mass/volume) of fuel is burnt completely, and the products of combustion are cooled to room temperature.

Usually all fuels contain hydrogen. During combustion, the hydrogen present in the fuel is converted into steam. When the combustion products are cooled to room temperature, the steam gets condensed into water and heat that equals the latent heat of condensation of steam is evolved. This heat gets included in the measured heat, and so its value is high; hence, it is called higher calorific value.

Low Calorific Value (LCV) It is also termed as net calorific value (NCV) and is defined as the heat produced when a unit quantity (mass/volume) of a fuel is burnt completely and the hot combustion products are allowed to escape.

In actual practice, when a fuel is burnt water vapor escapes along with the hot combustion gases; hence, heat available is lesser than the gross calorific value. Therefore, this is called low calorific value or net calorific value.

Thus $LCV = HCV - \text{Latent heat of water vapour formed.}$

As 1 part by weight of hydrogen gives 9 parts by weight of water,



$$LCV = HCV - \text{Weight of hydrogen in unit mass/volume of fuel} \times 9 \times \text{latent heat of steam}$$

Solved Examples

- 2 kg of a coal sample was burnt in a bomb calorimeter. The heat liberated was estimated and found to be 14114 kcal. Calculate the calorific value of the coal sample.

Solution

Heat liberated on burning 2 kg coal = 14,114 kcal.

Therefore, heat liberated on combustion of 1 kg coal = $\frac{14114}{2} = 7057$ kcal.

[Ans Calorific value of coal = 7057 kcal/kg]

- The gross calorific value of a fuel containing 8% hydrogen was found to be 9225.9 kcal/kg. Find out its net calorific value if the latent heat of steam is 587 kcal/kg.

Solution

$NCV = GCV - 0.09 H \times \text{Latent heat of steam (H = \% of hydrogen in fuel).}$

$NCV = 9225.9 - 0.09 \times 8 \times 587.$

$= 9225.9 - 422.64 = 8803.26$ kcal/kg

[Ans LCV/NCV = 8803.26 kcal/kg]

Practice problems

1. Calculate the GCV of a coal sample if its LCV is 6767.45 cal/g and if it contains 5% hydrogen. (Latent heat of steam is 587 cal/g).

[Ans GCV = 7031.6 cal/g]

2. The gross calorific value of a fuel containing 6% H was found to be 9804.6 kcal/kg. Find the net calorific value if the latent heat of steam is 587 cal/g.

[Ans 9487.62 kcal/kg]

1.5 Determination of Calorific Value

The calorific value of solid and non-volatile liquid fuels is determined by bomb calorimeter, whereas the calorific value of gaseous fuels is determined by Junkers calorimeter.

Bomb calorimeter

Principle A known amount of fuel is burnt in excess of oxygen and the heat liberated is absorbed in a known amount of water. This heat liberated is measured by noting the change in temperature. Calorific value of the fuel is then calculated by applying the following principle:

Heat liberated by fuel = Heat absorbed by water and the calorimeter.

Construction A simple sketch of the bomb calorimeter is shown in the Figure 1.2.

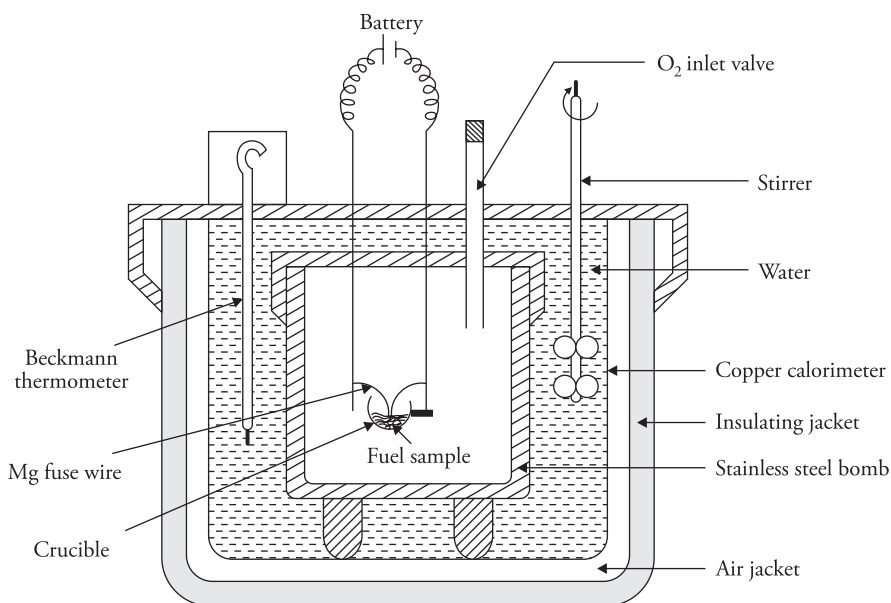


Figure 1.2 Bomb calorimeter

It consists of the following parts:

- (i) **Stainless Steel Bomb** It consists of a long cylindrical container made up of stainless steel. It has a lid that is made air tight with the help of screws. The lid is provided with two holes for electrodes and has an oxygen inlet valve. A small ring is attached to one of the electrodes. This ring acts as a support for nickel or stainless steel crucible in which the fuel is burnt. Magnesium wire touching the fuel sample extends across the electrodes. The steel bomb is lined inside with platinum to resist corrosive action of HNO_3 and H_2SO_4 vapors formed because of burning of fuel and is designed to withstand high pressure (25–50 atm).
- (ii) **Copper Calorimeter** The bomb is placed in a copper calorimeter containing a known amount of water. The calorimeter is provided with an electrical stirrer and a Beckmann thermometer that can read accurate temperature difference of up to $1/100^{\text{th}}$ of a degree.
- (iii) **Air Jacket and Water Jacket** The copper calorimeter is surrounded by an air jacket and a water jacket to prevent loss of heat owing to radiation.

Working A known amount of fuel (0.5–1 g) is taken in a clean crucible supported over the ring. A fine magnesium wire, touching the fuel sample, is then stretched across the electrodes. About 10 mL of distilled water is introduced into the bomb to absorb vapors of sulphuric acid and nitric acid formed during combustion, and the lid of the bomb is tightly screwed. The bomb is filled with oxygen at 25 atmospheric pressure and placed in the copper calorimeter containing a known weight of water. The stirrer is started and the initial temperature of water is noted. The electrodes are then connected to a 6-volt battery to complete the circuit. The sample burns and heat is liberated. This heat is absorbed by water. Maximum temperature shown by the thermometer is recorded. Time taken to cool the water in the calorimeter from maximum temperature to room temperature is also noted. The gross calorific value of the fuel is calculated as follows.

Calculations

Let

Weight of fuel sample taken	= x g
Weight of water in the calorimeter	= W g
Water equivalent* of calorimeter, stirrer, thermometer, bomb etc	= w g
Initial temperature of water in the calorimeter	= $t_1^\circ\text{C}$
Final temperature of water in the calorimeter	= $t_2^\circ\text{C}$
Higher calorific value of fuel	= H calorie / g
Heat liberated by burning of fuel	= $x \times H$
Heat gained by water	= $W \times \Delta T \times \text{specific heat of water}$ = $W (t_2 - t_1) \times 1 \text{ cal}$
Heat gained by calorimeter	= $w (t_2 - t_1)$
Total heat gained	= $W (t_2 - t_1) + w (t_2 - t_1)$ = $(W + w) (t_2 - t_1)$

* Water equivalent of a calorimeter is the product of mass of calorimeter and its specific heat. It is constant for a particular instrument.

But

Heat liberated by the fuel = Heat absorbed by water and calorimeter.

$$x \times H = (W + w) (t_2 - t_1)$$

$$H = \frac{(W + w)(t_2 - t_1)}{x} \text{ cal/g (or kcal/kg)}$$

Net (lower) calorific value

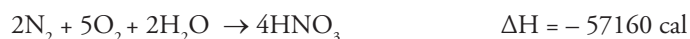
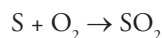
$$\text{LCV} = \text{HCV} - 0.09 H \times 587 \text{ cal/g or kcal/kg}$$

(Latent heat of condensation of steam = 587 kcal/kg).

Corrections

The following corrections are applied to get more accurate results

- (a) **Fuse Wire Correction** The gross calorific value calculated above includes the heat liberated by the ignition of Mg fuse wire; hence, this amount of heat has to be subtracted from the total value.
- (b) **Acid Correction** During combustion, sulphur and nitrogen present in the fuel get oxidised to H_2SO_4 and HNO_3 , respectively:



Hence, the formation of acids is exothermic and this should be subtracted from the obtained value of GCV.

- (c) **Cooling Correction** Heating and cooling are simultaneous processes. As the temperature rises above the room temperature, the loss of heat occurs due to radiation and the highest temperature recorded will be slightly less than that obtained if there was no heat loss. A temperature correction (cooling correction) is therefore necessary to get the correct rise in temperature.

If the time taken for the water in the calorimeter to cool from maximum temperature attained to room temperature is 'x' minutes and the rate of cooling is dt/min, then the cooling correction is $x \times dt$ and this is to be added to the rise in temperature.

$$\text{HCV of fuel (H)} = \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{Acid} + \text{fuse wire correction})}{\text{Mass of the fuel}(x)}$$

Solved examples

1. 0.72 g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 °C to 29.1 °C. If the calorimeter contains 250 g of water and its water equivalent is 150 g, calculate the HCV of the fuel. Give your answer in kJ/kg.

Solution

Here $x = 0.72$ g, $W = 250$ g, $w = 150$ g, $t_1 = 27.3$ °C, $t_2 = 29.1$ °C

Therefore, HCV of fuel (H) = $\frac{(W + w)(t_2 - t_1)}{x}$ cal/g

$$\frac{(250 + 150)(29.1 - 27.3)}{0.72} \text{ cal/g} = 1000 \times 4.18 \text{ J/g} = 4180 \text{ J/g} = 4180 \text{ kJ/kg}$$

(1 cal = 4.18 Joules).

2. On burning 0.83 g of a solid fuel in a bomb calorimeter, the temperature of 3500 g of water increased from 26.5 °C to 29.2 °C. Water equivalent of calorimeter and latent heat of steam are 385.0 g and 587.0 cal/g, respectively. If the fuel contains 0.7% hydrogen, calculate its gross and net calorific values.

Solution

Here, Weight of fuel (x) = 0.83 g; weight of water (W) = 3500 g; water equivalent of calorimeter (w) = 385 g; $(t_2 - t_1) = (29.2$ °C $- 26.5$ °C) = 2.7 °C; percentage of hydrogen (H) = 0.7%; Latent heat of steam = 587 cal/g.

$$\text{HCV of fuel (H)} = \frac{(W + w)(t_2 - t_1)}{x} \text{ cal/g} = \frac{(3500 + 385) \times 2.7}{0.83} = 12,638 \text{ cal/g}$$

Net calorific value = $(\text{HCV} - 0.09 \text{ H} \times 587) = (12638 - 0.09 \times 0.7 \times 587) \text{ cal/g}$.

$$= (12,638 - 37) \text{ cal/g} = 12,601 \text{ cal/g}$$

3. A coal sample contains: C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in a bomb calorimeter:

- (i) Wt of coal burnt = 0.92 g
- (ii) Wt of water taken = 550 g
- (iii) Water equivalent of bomb and calorimeter = 2200 g
- (iv) Rise in temperature = 2.42 °C
- (v) Fuse wire correction = 10.0 cal
- (vi) Acid correction = 50.0 cal

Calculate the gross calorific value of the coal.

Solution

Wt of coal (x) = 0.92 g;

Wt of water taken (W) = 550 g

Water equivalent of bomb and calorimeter (w) = 2200 g

Rise in temperature ($t_2 - t_1$) = 2.42 °C;

Fuse wire correction = 10.0 cal

Acid correction = 50.0 cal; latent heat of condensation of steam = 580 cal/g;

Percentage of hydrogen = 6%

$$\begin{aligned} \text{GCV} &= \frac{(W + w)(t_2 - t_1) - (\text{Acid} + \text{fuse wire correction})}{x} \\ &= \frac{(550 + 2200) \times 2.42 - (50 + 10)}{0.92} = 7168.5 \text{ cal/g} \end{aligned}$$

4. A coal sample contains C = 92%, H = 5% and ash = 3%. When this coal sample was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained

Wt of coal burnt = 0.95 g

Wt of water taken = 700 g

Water equivalent of bomb and calorimeter = 2000 g

Rise in temperature = 2.48 °C

Fuse wire correction = 10.0 cal

Acid correction = 60.0 cal

Cooling correction = 0.02 °C

Calculate the gross and net calorific value of the coal sample in cal/g. Assume the latent heat of condensation of steam as 580 cal/g.

Solution

$$\begin{aligned} \text{GCV} &= \frac{(W + w)(t_2 - t_1 + \text{cooling correction}) - (\text{acid correction} + \text{fuse wire correction})}{\text{weight of coal sample taken}} \\ &= \frac{(2000 + 700)(2.48 + 0.02) - (10 + 60)}{0.95} = \frac{(2700)(2.50) - (70)}{0.95} \\ &= \frac{6750 - 70}{0.95} = \frac{6680}{0.95} = 7031.57 \text{ cal/g} \end{aligned}$$

$$\text{LCV or NCV} = \text{HCV} - 0.09 \text{ H} \times 580 \text{ cal/g}$$

$$= 7031.57 - 0.09 \times 5 \times 580$$

$$= 7031.57 - 261 = 6770.57 \text{ cal/g}$$

$$[\text{Ans} \quad \text{HCV/GCV} = 7031.57 \text{ cal/g}]$$

$$\text{LCV/NCV} = 6770.57 \text{ cal/g}]$$

Practice problems

1. The temperature of 950 g of water was increased from 25.5 °C to 28.5 °C on burning 0.75 g of a solid fuel in a bomb calorimeter. Water equivalent of calorimeter and latent heat of steam are 400 g and 587 cal/g, respectively. If the fuel contains 0.65% of hydrogen, calculate its net calorific value.

[Ans 5365.66 cal/g]

2. Liquid fuel weighing 0.98 g and containing 90.1% C, 8% H and having the following results in bomb calorimeter experiment

Amount of water taken in calorimeter = 1450 g

Water equivalent of calorimeter = 450 g

Rise in temperature of water = 1.8 °C

If the latent heat of steam is 587 cal/g, calculate gross and net calorific value of fuel.

[Ans GCV = 3489.79 cal/g; LCV = 3067.15 cal/g]

Calorific Value of Gaseous Fuels

Junker's Gas Calorimeter It is used for measuring the calorific value of gaseous and volatile liquid fuels.

Principle A known volume of gas is burnt at known pressure in a small enclosed combustion chamber. The heat liberated is absorbed by water flowing at constant rate through the water jacket. By knowing the initial and final temperatures of water, the quantity of water and weight of water condensed, the calorific value can be determined.

Construction

It consists of the following parts:

1. **Bunsen Burner** It is used for the combustion of gaseous fuel. It is clamped at the bottom and can be pulled out or pushed into the chamber during combustion.
2. **Gasometer** It measures the volume of the gas burning per unit time. It is attached with a manometer fitted with a thermometer to record the pressure and temperature of the gas before burning.
3. **Pressure Governor** It regulates the supply of a gaseous fuel at constant pressure.
4. **Gas Calorimeter** It consists of a vertical cylindrical combustion chamber where combustion of gaseous fuel is carried out. The combustion chamber is surrounded by an annular water space where water is made to circulate. Loss of heat by radiation and convection is prevented by an outer jacket, which is chromium-plated. Moreover, the outer jacket contains air that is a very good heat insulator. There are openings at appropriate places where thermometers are placed for measuring the temperature of the inlet and outlet water.

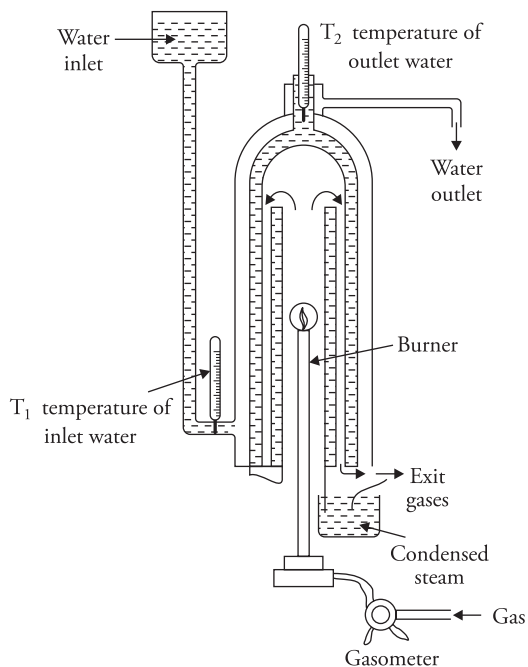


Figure 1.3 Junker's gas calorimeter

Working A known volume of gas is burnt at a constant rate in a combustion chamber in the presence of excess air. All the heat produced is absorbed by water circulating in the annular space around the combustion chamber.

Observations

- (i) The volume of gaseous fuel burnt at a given temperature and pressure in a certain time = $V \text{ m}^3$
- (ii) Weight of water circulated through the coils in time $t = W \text{ g}$
- (iii) Temperature of inlet water = $t_1 \text{ }^\circ\text{C}$
- (iv) Temperature of outlet water = $t_2 \text{ }^\circ\text{C}$
- (v) Weight of steam condensed in time t in a graduated cylinder = $m \text{ kg}$.

Let GCV of the fuel = H

Heat produced by the combustion of fuel = $V \times H$

Heat absorbed by circulating water = $W (t_2 - t_1)$

Assuming no loss of heat,

$$V \times H = W (t_2 - t_1)$$

HCV or GCV

$$H = \frac{W(t_2 - t_1)}{V} \text{ kcal/m}^3$$

Weight of steam condensed in a certain time t by the combustion of $V \text{ m}^3$ of the fuel = $m \text{ kg}$

Mass of H_2O condensed per m^3 of the fuel = $m/V \text{ kg}$

$$\text{Latent heat of steam per m}^3 \text{ of the fuel} = \frac{m \times 587}{V} \text{ kcal},$$

$$\text{therefore, NCV or LCV} = \left[H - \frac{m \times 587}{V} \right] \text{ kcal/m}^3$$

Boy's Gas Calorimeter

Like Junker's calorimeter, the Boy's gas calorimeter is also used to find the calorific value of gaseous and volatile liquid fuels. It consists of the following parts.

1. **Gas Burner** Gas burner is used for the combustion of a known volume of gas at a known pressure. The volume of the gas burnt is measured with the help of a gasometer and the pressure of the gas is monitored using pressure governor.
2. **Combustion Chamber** The combustion chamber or chimney has copper tubes coiled inside and outside the combustion chamber. Water circulates in these coils. It enters from the top of the outer coil, passes through the outer coils, moves to the bottom of the chimney and then moves upwards through the inner coil and exits from the top.

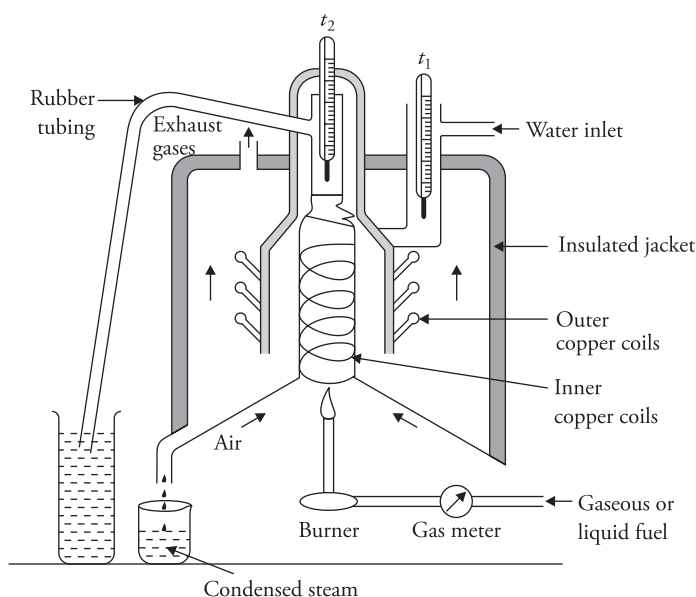


Figure 1.4 Boy's gas calorimeter

3. **Thermometers** Two thermometers t_1 and t_2 measure the temperatures of the incoming and outgoing water.
4. A graduated beaker is placed at the bottom to collect the condensed steam produced during combustion.

Working The working is similar to Junker's calorimeter. The water is circulated and the fuel is burnt to provide an initial warming period of 15 minutes. When the calorimeter is warmed, the rate of flow of the gas is adjusted and it is burnt inside the calorimeter. The heat produced by the combustion is absorbed by water circulating in the copper tubes. The rise in temperature, volume of gas burnt, volume of water circulated in the coils in time t and the mass of steam condensed help in finding the calorific value of the given fuel sample (for observation and calculation refer Junker's calorimeter).

Solved Examples

1. The following data were obtained in a Junker's calorimeter experiment:

Volume of gas used	= 0.1 m ³ at STP
Wt of water heated	= 25 kg
Temperature of inlet water	= 20 °C
Temperature of outlet water	= 33 °C
Weight of steam condensed	= 0.025 kg

Calculate the higher and lower calorific value per m³ at STP. Take the heat liberated in condensing water vapours and cooling the condensate as 580 kcal/kg.

Solution

Here,

$$V = 0.1 \text{ m}^3; W = 25 \text{ kg}; T_2 = 33 \text{ }^\circ\text{C}; T_1 = 20 \text{ }^\circ\text{C}; m = 0.025 \text{ kg}.$$

$$\text{Therefore, HCV(H)} = \frac{W(T_2 - T_1)}{V} = \frac{25(33 - 20)}{0.1 \text{ m}^3} = 3250 \text{ kcal/m}^3.$$

$$\begin{aligned} \text{And LCV} &= \text{HCV} - (m/V) \times 580 \\ &= 3250 \text{ kcal/m}^3 - [(0.025 \text{ kg} / 0.1 \text{ m}^3) \times 580 \text{ kcal/kg}]. \\ &= 3250 \text{ kcal/m}^3 - 145 \text{ kcal/m}^3 = 3105 \text{ kcal/m}^3. \end{aligned}$$

Practice problems

1. During the determination of calorific value of a gaseous fuel by Boy's calorimeter, the following results were recorded:
 - Volume of gaseous fuels burnt at NTP = 0.098 m³
 - Weight of water used for cooling the combustion products = 50 kg
 - Weight of steam condensed = 0.051 kg
 - Temperature of inlet water = 26.1 °C

Temperature of outlet water = 46.5 °C

Latent heat of condensation of steam = 587 kcal/kg

Determine the gross and net calorific values.

[Ans HCV/GCV = 10408.2 kcal/m³; NCV/LCV = 10102.7 kcal/m³]

Theoretical Calculation of Calorific Value of a Fuel

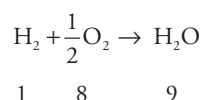
Dulong's assumed that the heat evolved comes from the combustion of carbon, hydrogen and sulphur present in the fuel, and the calorific value of the fuel is the sum of the calorific values of these constituents.

The calorific values of C, H and O are found to be 8080, 34500 and 2240 kcal/kg, respectively.

Constituent	Higher calorific value
C	8080 kcal/kg
H	34500 kcal/kg
S	2240 kcal/kg

If oxygen is also present, it combines with hydrogen to form H₂O. Thus, the hydrogen in combined form is not available for combustion and is called fixed hydrogen.

Amount of hydrogen available for combustion = Total mass of hydrogen–hydrogen combined with oxygen.



that is 8 parts of oxygen combines with 1 part of hydrogen to form water or for every 8 parts of oxygen, 1 part of hydrogen gets fixed.

If the fuel contains x mass of oxygen then

$$\text{Fixed hydrogen} = \frac{1}{8} \times x = \frac{\text{Mass of oxygen in fuel}}{8}$$

$$\text{Amount of hydrogen available for combustion} = \left(\text{H} - \frac{\text{O}}{8} \right)$$

Dulong's formula for calculating calorific value is given as

$$\text{Gross calorific value (HCV)} = \frac{1}{100} \left[8080C + 34500 \left(\text{H} - \frac{\text{O}}{8} \right) + 2240S \right] \text{ kcal/kg}$$

Here C, H, O and S are percentages of carbon, hydrogen, oxygen and sulphur in fuel.

$$\text{Net calorific value (LCV)} = \left(\text{HCV} - \frac{9\text{H}}{100} \times 587 \right) \text{ kcal/kg}$$

$$(\text{HCV} - 0.09 \text{H} \times 587) \text{ kcal/kg}$$

(Latent heat of steam = 587 kcal/kg).

Solved Examples

Calculate the gross and net calorific values of coal having the following composition:

Carbon = 85%; hydrogen = 8%; sulphur = 1%; nitrogen = 2%; ash = 4%

Latent heat of steam = 587 cal/g.

Solution

$$\text{Gross calorific value (HCV)} = \frac{1}{100} \left[8080C + 34500 \left(H - \frac{O}{8} \right) + 2240S \right] \text{ kcal/kg}.$$

$$\% \text{ Oxygen} = 100 - \% (C + H + S + N + \text{ash})$$

$$= 100 - (85 + 8 + 1 + 2 + 4) = 0$$

$$= \frac{1}{100} \left[8080 \times 85 + 34500 \left(8 - \frac{0}{8} \right) + 2240 \times 1 \right] \text{ kcal/kg}$$

$$= \frac{1}{100} [686,800 + 276,000 + 2240] \text{ kcal/kg}$$

$$= \frac{1}{100} [965040] \text{ kcal/kg} = 9650.4 \text{ kcal/kg}$$

$$\text{LCV} = (\text{HCV} - 0.09 H \times 587) \text{ kcal/kg}$$

$$(9650.4 - 0.09 \times 8 \times 587) \text{ kcal/kg} = 9227.76 \text{ kcal/kg}.$$

Practice problems

1. A sample of coal has the following composition:
Carbon = 83%; hydrogen = 7.5%; sulphur = 1.5%; nitrogen = 0.6%; oxygen = 8.4%
Find the gross calorific value using Dulong formula.

[Ans = 8965.25 kcal/kg]

2. Calculate the gross and net calorific value of coal having the following composition
Carbon = 80%; hydrogen = 7%; sulphur = 3.5%; nitrogen = 2.1%; ash = 4.4%
Latent heat of steam = 587 kcal/kg.

[Ans (i) 8828.02 kcal/kg; (ii) 8458.21 kcal/kg]

1.6 Solid Fuels

Solid fuel refers to various types of solid materials that are used as fuel to produce energy. The primary solid fuels commonly used are wood and coal.

Wood Wood is being used as fuel from times immemorial. Freshly cut wood contains 25 to 50% moisture which reduces to 15% after drying the wood in air. The average composition of wood is: C = 55%; H = 6%; O = 43%; ash = 1%. Its calorific value is about 3500–4500 kcal/kg. It burns

with a long and non-smoky flame leaving behind small amount of ash. Destructive distillation of wood at around 500 °C produces charcoal which is an excellent fuel equivalent to the best of fuels.

Coal Coal is produced when the plant and animal debris are subjected to conditions of high temperature and pressure over millions of years. Hence, it is regarded as a fossil fuel. It chiefly comprises C, H, N and O besides non-combustible matter.

Classification and rank of coal

The different types of coal in increasing order of alteration are peat, lignite (brown coal immature), sub-bituminous, bituminous and anthracite (mature). Coal starts off as **peat**. After being subjected to heat and pressure for a considerable amount of time, it is metamorphosed from peat to **lignite**. Lignite is referred to as brown coal because it is somewhat light in color and it remains soft. As time passes, lignite increases in maturity by becoming darker and harder and is then classified as **sub-bituminous** coal. As this process of burial and alteration continues, more chemical and physical changes occur and the coal is classified as **bituminous**. At this point the coal is dark and hard. **Anthracite** is the last stage of coal formation. Anthracite coal is very hard and shiny.

Table 1.2 Percentage composition of solid fuels (dry ash free basis)

Fuel	Moisture of air dried sample at 40 °C (%)	C (%)	H (%)	N (%)	O (%)	Calorific value (kcal/kg)
Wood	25	50.0	6.0	0.5	43.5	4000–4500
Peat	25	57.0	5.7	2.0	35.3	4125–5400
Lignite	20	67.0	5.0	1.5	26.5	6500–7100
Sub-bituminous coal	11	77.0	5.0	1.8	16.2	7000–7500
Bituminous coal	4	83.0	5.0	2.0	10.0	8000–8500
Semi-bituminous coal	1	90.0	4.5	1.5	4.0	8350–8500
Anthracite	1.5	93.3	3.0	0.7	3.0	8650–8700

1.7 Analysis of Coal

The composition of coal varies widely. It is necessary to analyse and interpret the results for the purpose of price fixation, commercial classification and proper industrial utilisation.

The quality of coal is ascertained by two types of analysis:

- Proximate analysis
- Ultimate analysis

Proximate Analysis

It is an empirical but important analysis dealing with the determination of moisture content, volatile matter, ash content and fixed carbon. It is called proximate analysis because the data vary with the procedure adopted. This analysis provides data for a general assessment of the quality and type of coal. It involves the following determinations:

1. Moisture Content

A known weight of coal (air-dried) is taken in a crucible and heated in an electric hot air oven at about 105 °C–110 °C for about one hour. After 1 hour, it is taken out from the oven and cooled in a dessicator and weighed. Loss in weight of the sample is found out and the percentage of moisture is calculated as follows:

Let the weight of coal sample = W g

Weight after heating for 1 h = W_1 g

Loss in weight, that is the weight of moisture = $(W - W_1)$ g

$$\% \text{ Moisture} = \frac{(W - W_1)}{W} \times 100$$

$$= \frac{\text{Loss in weight of the sample or weight of moisture}}{\text{Weight of coal sample taken}} \times 100.$$

Significance

- High moisture content is undesirable because it reduces the calorific value and increases the transportation cost.
- Presence of excessive moisture quenches fire in the furnace.
- A considerable amount of heat is wasted in evaporating the moisture during combustion.

2. Volatile Matter

The volatile matter present in the coal may be combustible gases such as H_2 , CO , CH_4 and other hydrocarbons or non-combustible gases such as CO_2 and N_2 . It *does not* include moisture of the coal.

It is determined by heating a known weight of moisture-free coal in a silica crucible covered with a vented lid at 950 ± 20 °C for 7 minutes in a muffle furnace. The crucible is then taken out and cooled inside a dessicator and weighed again. Complete removal of volatile matter is judged by bubbling the gas through a water seal. Loss in weight gives the weight of the volatile matter and the percentage of volatile matter is calculated as follows:

Let the weight of sample after removal of volatile matter = W_2 g

Weight of volatile matter = $(W_1 - W_2)$ g.

$$\% \text{ Volatile matter} = \frac{(W_1 - W_2)}{W} \times 100$$

$$= \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

It may be noted here that it is not correct to say coal with 20% volatile matter or coal containing 20% volatile matter because volatile matter is not present as such in coal but it is the product of thermal decomposition of coal; hence, it should be accurately described as coal yielding 20% volatile matter although the former term is widely used in coal analysis.

Significance

- Coal containing high percentage of volatile matter burns with a long flame and high smoke and has low calorific value. Coals with high percentage of volatile matter ignite easily but burn very quickly.
- A high percentage of volatile matter indicates that a large proportion of fuel is burnt as gas.
- Presence of non-combustible gases is undesirable since they do not add to the heat value.
- For efficient use of fuel, the outgoing combustible gas (volatile matter) has to be burnt by supplying secondary air. This requires a large combustion space.
- If the furnace volume is small or flame is short, a large proportion of volatile matter will escape unburnt.
- Coals with higher percentage of volatile matter do not cake well, whereas medium volatile coals containing 20–30% of volatile matter are capable of forming hard and strong coke on carbonisation.
- Low volatile matter containing coals do not cake at all and are thus unsuitable for coke making.
- High volatile matter is desirable in coal gas manufacture because volatile matter in a coal denotes the proportion of coal that will be converted into gas and tar products by heat.
- However, for the manufacture of metallurgical coke, coal with low volatile matter content is preferred.

3. Ash

Ash is the non-combustible, useless matter that is left behind when all the combustible substances have burnt off from coal. Ash usually consists of silica, alumina, iron oxide and small quantities of lime, magnesia, etc.

Ash content is determined by heating the residue obtained after removal of moisture and volatile matter at $700 \pm 50^\circ\text{C}$ for half an hour without a lid in muffle furnace. The residue left is cooled in a dessicator and weighed. From the weight of residue, the percentage of ash is calculated as

Let the weight of ash formed = W_3 g.

$$\begin{aligned}\% \text{ ash} &= \frac{W_3}{W} \times 100 \\ &= \frac{\text{Weight of ash formed}}{\text{Weight of coal sample taken}} \times 100\end{aligned}$$

Significance

- High percentage of ash is undesirable as it reduces the calorific value of the fuel.
- Presence of ash increases the transporting, handling and storage cost.
- It also involves additional cost of ash disposal.
- Fused ash lumps (clinkers) block the interspaces of the grate on which coal is being burnt. This causes obstruction in air supply. Hence, burning of coal becomes irregular. Hence, lower the ash content better the quality of the coal.

4. Fixed Carbon

Fixed carbon is the material remaining after determination of moisture, volatile matter and ash content. It is determined indirectly by the formula:

Percentage of fixed carbon = $100 - \text{percentage of (moisture + volatile matter + ash)}$.

Significance

- Higher the percentage of fixed carbon, greater is the calorific value.
- Coals with high fixed carbon content are difficult to ignite but they burn slowly.
- The percentage of fixed carbon helps in designing the furnace because it is the fixed carbon that burns in the solid state.

Solved Examples

A sample of coal was analysed as follows. Exactly 2.5 g was weighed into a silica crucible. After heating for an hour at 110°C , the residue weighed 2.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at $950 \pm 20^\circ\text{C}$. The residue weighed 1.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 g. Calculate the percentage of moisture, volatile matter, ash and fixed carbon in the coal sample.

Solution

(i) *Percentage of moisture*

Weight of coal sample taken = 2.5 g

Weight after heating at 110°C = 2.415 g

Loss of weight = weight of moisture = $2.500 - 2.415 = 0.085$ g

$$\% \text{ moisture} = \frac{\text{weight of moisture}}{\text{weight of coal taken}} \times 100$$

$$= \frac{0.085}{2.500} \times 100 = 3.4\%$$

% moisture = 3.4%

(ii) *Percentage of volatile matter*

Weight of residue after heating at 950 °C = 1.528 g

Loss of weight = weight of volatile matter = 2.415 – 1.528 = 0.887 g.

$$\begin{aligned}\% \text{ volatile matter} &= \frac{\text{weight of volatile matter}}{\text{weight of coal sample taken}} \times 100 \\ &= \frac{0.887}{2.500} \times 100 = 35.48\end{aligned}$$

% volatile matter = 35.48%

(iii) *Percentage of ash*

$$\frac{\text{weight of residue left}}{\text{weight of coal sample taken}} \times 100$$

$$\frac{0.245}{2.5} \times 100 = 9.8\%$$

% ash = 9.8%

(iv) *Percentage of fixed carbon* = 100 – percentage of (moisture + volatile matter + ash)

$$= 100 - (3.4 + 35.48 + 9.8)$$

$$= 100 - 48.68 = 51.32\%$$

% fixed carbon = 51.32%

Practice problems

1. A sample of coal was analysed as follows:

Exactly 1.5 g was weighed into a silica crucible. After heating for an hour at 110 °C, the residue weighed 1.415 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20 °C. The residue weighed 0.528 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.254 g. Calculate

- The percentage results of the above analysis.
- To which type of analysis does the above description belong? Why the above analysis is named so?

[Ans Moisture = 5.67%; volatile matter = 59.13%; ash = 16.93%;
fixed carbon = 18.27%]

2. A sample of coal was analysed as follows:

Exactly 2.000 g was weighed into a silica crucible. After heating for an hour at 110 °C, the residue weighed 1.975 g. The crucible was then covered with a vented lid and strongly heated for exactly 7 min at 950 ± 20 °C. The residue weighed 1.328 g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.204 g. Calculate

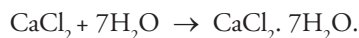
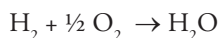
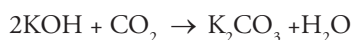
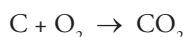
The percentage results of the above analysis.

[Ans Moisture = 1.25%; volatile matter = 32.35%; Ash = 10.20%;
fixed carbon = 56.20%]

Ultimate Analysis

It is also called elemental analysis and is used for the determination of carbon, hydrogen, nitrogen, sulphur and oxygen. This analysis requires high degree of skill and the equipments are expensive. However, it gives exact results that are useful in calculating the calorific value of coal using *Dulong's formula*.

1. **Carbon and Hydrogen** Carbon in coal sample occurs in combined form in complex organic matter and can also be present as mineral carbonates. Hydrogen on the other hand is found in organic matter in coal and is also found associated with the moisture present in coal. To estimate carbon and hydrogen accurately weighed coal sample is burnt in a combustion tube in a current of O₂ (free from CO₂ and moisture). The carbon and hydrogen present in the fuel is converted to CO₂ and H₂O, respectively. These are then absorbed by previously weighed tubes containing KOH and anhydrous CaCl₂. The increase in weights of these tubes gives the amount of CO₂ and H₂O formed. The percentage of C and H is then calculated as follows



Let the weight of coal sample taken = x g.

Increase in weight of KOH tube = y g.

Increase in weight of CaCl₂ tube = z g.

Now,

44 g of CO₂ contains 12 g of C.

y g of CO₂ contains $\frac{12}{44} \times y$ g of C.

Percentage of carbon = $\frac{12}{44} \times \frac{y}{x} \times 100$

or percentage of carbon = $\frac{12}{44} \times \frac{\text{Increase in weight of KOH tube}}{\text{weight of coal sample taken}} \times 100$

Similarly,

18 g of H_2O contains 2 g of H

z g of H_2O contains $\frac{2 \times z}{18}$ g of H

Percentage of hydrogen = $\frac{2}{18} \times \frac{z}{x} \times 100$

Percentage of hydrogen = $\frac{2}{18} \times \frac{\text{Increase in weight of CaCl}_2 \text{ tube}}{\text{Weight of coal sample taken}} \times 100$

Significance

- Calorific value of a fuel is directly related to the carbon content; hence, greater the percentage of carbon, greater is the calorific value of the fuel.
- Percentage of carbon increases from lignite to anthracite; thus, the percentage of carbon forms the basis of classification of coal.
- High percentage of hydrogen also increases the calorific value of coal. However, hydrogen is mostly associated with volatile matter and affects the use to which coal is put.
- In carbonisation and gasification industries, hydrogen of coal is responsible for the production of many useful materials such as gaseous hydrogen, methane, etc.

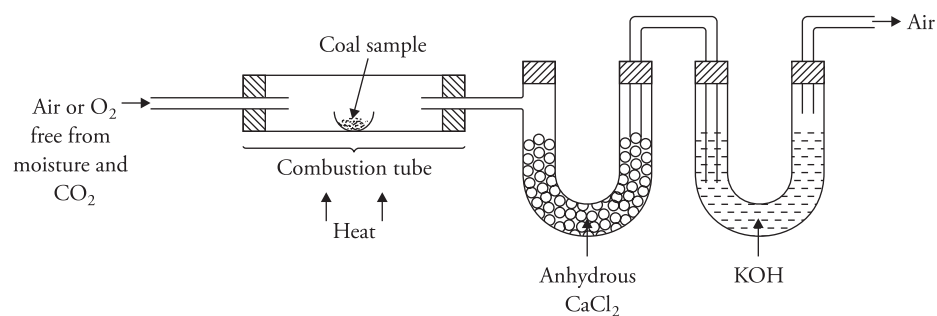
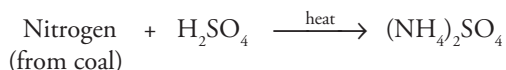


Figure 1.5 Determination of carbon and hydrogen

2. **Nitrogen** All the nitrogen present in coal is assumed to occur within the organic matter of coal. Nitrogen present in coal sample is estimated by Kjeldahl's method.

- Accurately weighed coal sample is heated with concentrated H_2SO_4 in the presence of K_2SO_4 in a long-necked flask known as Kjeldahl's flask. Nitrogen present in the coal gets converted to $(\text{NH}_4)_2\text{SO}_4$ quantitatively.



- When a clear solution is obtained (i.e., whole nitrogen is converted into ammonium sulphate), the contents are transferred into a round bottom flask and the solution is heated with excess of NaOH to liberate NH_3 .
- The NH_3 thus liberated is absorbed in a known volume of a standard H_2SO_4 solution (N/10).
- The volume of unused H_2SO_4 is determined by titrating against standard NaOH solution (N/10). Difference gives the volume of acid used. From the volume of acid used by NH_3 , the percentage of nitrogen can be calculated.

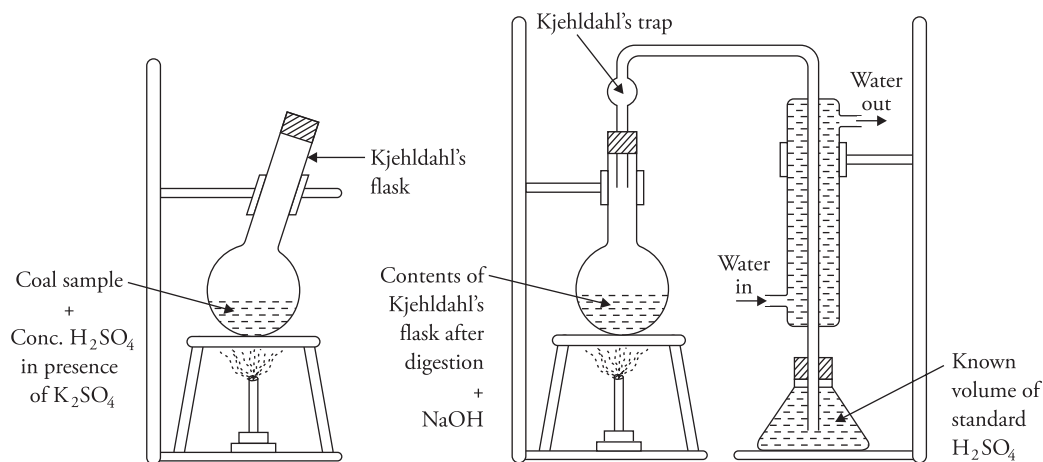
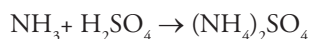
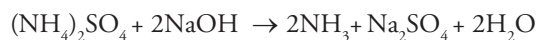


Figure 1.6 Estimation of nitrogen

Let the weight of coal taken = W g

Volume of acid used = V_1 mL

Normality of acid = N_1

As we know,

Equivalents of H_2SO_4 used = Equivalent of NH_3 formed

\therefore Equivalents of H_2SO_4 used = $N_1 V_1$

Hence, equivalents of NH_3 formed = $N_1 V_1$

Now,

Normal (1N solution of NH_3 means 1 g equivalent NH_3 dissolved in 1 liter water)

\therefore 1000 mL contains 17 g $\text{NH}_3 \equiv 14$ g nitrogen.

$N_1 V_1$ of NH_3 will contain = $\frac{14}{1000} \times N_1 V_1$ nitrogen.

$$\% \text{ Nitrogen} = \frac{14}{1000} \times \frac{N_1 V_1}{W} \times 100.$$

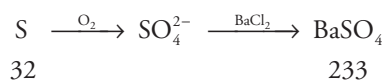
$$\% \text{ Nitrogen} = \frac{1.4 \times \text{Normality of } \text{H}_2\text{SO}_4 \times \text{Volume of } \text{H}_2\text{SO}_4 \text{ used}}{\text{Weight of coal sample taken}}$$

Significance

- Since nitrogen is an inert and incombustible gas with no calorific value, its presence in fuel is undesirable.

3. Sulphur

Sulphur is found in coal in three forms, as organic sulphur compounds, as inorganic sulphides and also as inorganic sulphates. To estimate the amount of sulphur in the coal sample a known amount of coal is burnt completely in a bomb calorimeter in a current of oxygen. Sulphur in the coal is oxidised to sulphates. The ash from the bomb calorimeter is extracted with dilute hydrochloric acid. The acid extract is then treated with BaCl_2 solution to precipitate sulphate as BaSO_4 . The precipitate of BaSO_4 is filtered, washed, dried and heated to a constant weight. From the weight of BaSO_4 formed, S is estimated as follows



Let the weight of coal sample = W g

Weight of $\text{BaSO}_4 = x$ g

\therefore 233 g of $\text{BaSO}_4 = 32$ g of S

$$\therefore x \text{ g of } \text{BaSO}_4 = \frac{32}{233} \times x$$

$$\% \text{ S} = \frac{32}{233} \times \frac{x}{W} \times 100$$

$$\text{or } \% \text{ S} = \frac{32}{233} \times \frac{\text{Weight of } \text{BaSO}_4}{\text{Weight of coal taken}} \times 100.$$

Significance

- Although sulphur increases the calorific value of fuel, yet its presence is undesirable because it gets oxidised to SO_2 and SO_3 , which causes environmental pollution.
 - Sulphur-containing coal is not suitable for preparing metallurgical coke. Presence of sulphur in coke used in the iron industry affects the quality and properties of steel.
4. **Ash** It is determined in the same way as in proximate analysis.
5. **Oxygen** It occurs both in organic and inorganic portions of coal and is determined indirectly by deducting the % of C, H, N, S and ash from 100
- % of oxygen = $100 - \% \text{ of } (C + H + N + S + \text{ash})$.

Significance

- Oxygen is present in coal in combined form. It is present in association with hydrogen; hence, it reduces the hydrogen available for combustion.
- Moreover, high oxygen-containing coals have high inherent moisture and hence low calorific values.
- Calorific value decreases about 1.7% for every 1% increase in oxygen.

Thus, a good-quality coal should have low percentage of oxygen.

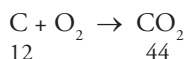
Solved examples

1. 0.25 g of a sample of coal was analysed by combustion method. The increase in weights of CaCl_2 tube and the potash bulbs at the end of the operation was found to be 0.15 g and 0.55 g, respectively. Calculate the percentage of carbon and hydrogen in the coal.

Solution

Weight of CO_2 (increase in weight of KOH bulb) = 0.55 g.

Weight of H_2O (increase in weight of CaCl_2 tubes) = 0.15 g.



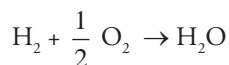
44 g CO_2 contains carbon = 12 g

0.55 g CO_2 contains carbon = $\frac{12}{44} \times 0.55$ g

$$\begin{aligned} \text{Percentage of carbon} &= \frac{12 \times \text{weight of carbondioxide}}{44 \times \text{weight of coal sample taken}} \times 100 \\ &= \frac{12}{44} \times \frac{0.55}{0.25} \times 100 = 60\% \end{aligned}$$

Percentage of carbon = 60%.

To calculate the percentage of hydrogen,



2 g 18 g

18 g H₂O contains hydrogen = 2 g

0.15 g H₂O contains hydrogen = $\frac{2}{18} \times 0.15$

Percentage of hydrogen = $\frac{2}{18} \times \frac{0.15}{0.25} \times 100 = 6.67\%$

Percentage of hydrogen = 6.67%

2. 1.0 g of a coal sample was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 8800 cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with BaCl₂ solution and a precipitate of BaSO₄ was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.08 g. Calculate the percentage of sulphur in the coal sample.

Solution

$$\begin{aligned} \text{Percentage of sulphur} &= \frac{\text{weight of BaSO}_4 \text{ ppt obtained} \times 32 \times 100}{233 \times \text{weight of coal sample taken}} \\ &= \frac{0.08 \times 32 \times 100}{233 \times 1} = 1.0987\% \end{aligned}$$

Percentage of sulphur = 1.0987%

3. 0.3 g of coal sample on Kjehldahl's analysis gave ammonia to just neutralise 30 mL of 0.1 N H₂SO₄. Calculate the percentage of nitrogen in the coal sample.

Solution

Weight of coal sample = 0.3 g

Volume of H₂SO₄ used = 30 mL

Normality of H₂SO₄ = 0.1 N

$$\begin{aligned} \text{Percentage of nitrogen} &= \frac{\text{volume of H}_2\text{SO}_4 \text{ used} \times \text{normality} \times 1.4}{\text{weight of coal sample taken}} \\ &= \frac{30 \times 0.1 \times 1.4}{0.3} = 14\% \end{aligned} \quad \text{Percentage of nitrogen} = 14\%$$

4. 1.56 g of a coal sample was Kjehldahlised and NH_3 gas thus evolved was absorbed in 50 mL of 0.1 N H_2SO_4 . After absorption, the excess (residual) acid required 6.25 mL of 0.1 N NaOH for exact neutralisation. Calculate the percentage of nitrogen in the coal sample.

Solution

Weight of coal sample taken = 1.56 g

Since 6.25 mL of 0.1N NaOH is used for neutralisation, excess acid

$$= 6.25 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4.$$

Therefore, volume of H_2SO_4 used to neutralise NH_3 evolved

$$= 50 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4 - 6.25 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$= (50 - 6.25) \times 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$= 43.75 \text{ mL of } 0.1 \text{ N } \text{H}_2\text{SO}_4$$

$$\text{Percentage of nitrogen} = \frac{\text{Volume of } \text{H}_2\text{SO}_4 \text{ used} \times \text{normality of } \text{H}_2\text{SO}_4 \times 1.4}{1.56} = 3.926\%$$

$$\frac{43.75 \times 0.1 \times 1.4}{1.56} = 3.926$$

$$\text{Percentage of nitrogen} = 3.926\%$$

Practice problems

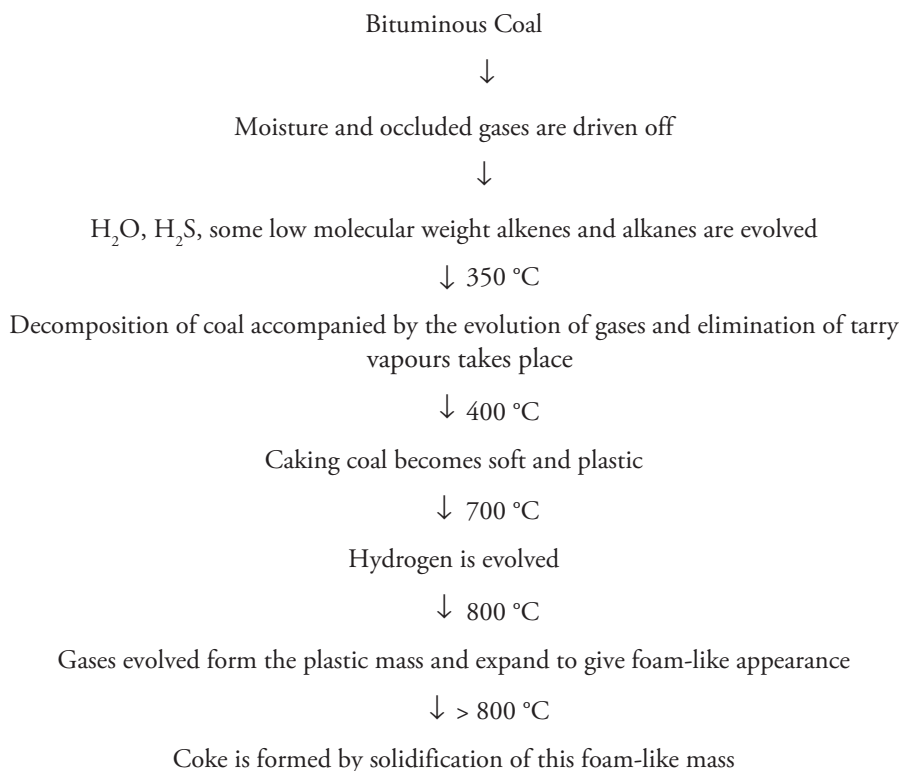
- 0.26 g of a sample of coal analysed by combustion gave 0.039 g of water and 0.245 g of carbon dioxide. Calculate the percentage of carbon and hydrogen in the coal.
[Ans % carbon = 25.69%; % hydrogen = 1.66%]
- 0.1 g of a sample of coal was used in a bomb calorimeter for the determination of calorific value. The ash formed was extracted with acid and the acid extract was heated with BaCl_2 solution and a precipitate of BaSO_4 was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.01 g. Calculate the percentage of sulphur in the coal sample.
[Ans % sulphur = 1.3734%]
- 3.12 g of the coal sample was Kjehldahlised and NH_3 gas was absorbed in 50 mL of 0.1N H_2SO_4 . After absorption, the excess (residual) acid required 12.5 mL of 0.1 N NaOH for exact neutralisation. Determine the percentage of nitrogen in the coal sample.
[Ans % nitrogen = 1.683%]
- 3.0 g of the coal sample was Kjehldahlised and NH_3 gas was absorbed in 45 mL of 0.1N H_2SO_4 . After absorption, the excess (residual) acid required 8.5 mL of 0.1 N NaOH for exact neutralisation. Determine the percentage of nitrogen in the coal sample.
[Ans % nitrogen = 1.7033%]

1.8 Carbonisation of Coal

When coal is heated to a high temperature in the absence of air, it loses volatile matter and gets converted into a white, dense, lustrous, strong, porous and coherent mass, which is richer in carbon content than the original fuel. This is known as *coke* and the process of converting coal into coke in the absence of air is known as *carbonisation of coal*.

Process of carbonisation

The process of carbonisation can be depicted with the help of the flow chart given below



Caking and coking coals

It is important to note that all types of coals cannot be converted into coke. Some coals soften and form a plastic mass that swells to a much larger volume than the original sample and resolidifies into a porous solid. Such coals are called *caking coals*. Only coals of bituminous rank display caking behaviour. When this porous solid is quenched, it results in the formation of a strong residue called coke. If the coke formed is hard, porous and strong, then the coal from which it is formed is called *coking coal*. Coking coal is also called metallurgical coke. This is a unique property of bituminous coal; hence, only bituminous coals can be converted into coke. Anthracite, sub-bituminous, lignite coals are non-caking coals. All coking coals are caking coals; however, only some caking coals fall under the category of coking coals.

Generally, coals with a high percentage of volatile matter, lower ash and higher fixed carbon content are not fit for 'coking'. The coals having 20–30% volatile matter are good coking coals.

Pulverised coal

Usually the rate of combustion of coal is very slow. This can be increased either by

- (i) Increasing the rate of supply of air; however, it results in the wastage of heat, as heat is carried away along with the current of air.
- (ii) Increasing the surface area of coal by powdering it. The powdered coal comes in contact with larger amount of oxygen and hence it burns readily.

This powdered coal is called pulverised coal. Generally, pulverisation is carried out for coals containing large amount of volatile matter. The volatile matter gets liberated out more quickly from the powder rather than from larger lumps of coal.

Advantages of pulverised coal

1. Its handling and transportation is easier. The transportation can be carried out by forcing a stream of air or by screw conveyor.
2. Combustion of pulverised coal is complete and uniform, as it gets intimately mixed with air.
3. The excess air needed for combustion is less than that needed for solid fuels.
4. The volatile matter is easily removed.
5. Rate of combustion can be controlled easily as in case of liquid and gaseous fuels.
6. There is no clinker formation in pulverised coal.

Disadvantages of pulverised coal

1. Additional cost is involved for pulverising and sieving the fuel.
2. The ash formed by burning of pulverised coal is in finely divided state. It is called 'Fly Ash' and it creates serious environmental problems.
3. Pulverised coal produces long flame and hence large combustion space is required.

Types of carbonisation

The properties of the coke produced depend on the type of coal used, temperature and the rate of carbonisation. Depending upon the temperature, carbonisation is of two types:

1. Low-temperature carbonisation
2. High-temperature carbonisation
 - (i) **Low temperature carbonisation** When destructive distillation of coal is carried out at 500–700 °C, it is called low temperature carbonisation. It is used mainly for the manufacture of domestic fuel.

The yield of coke is about 75–80%. The coke thus produced contains 5–15% volatile matter and is not strong enough to be used as metallurgical fuel. It is highly reactive, easily ignited and is a valuable, smokeless domestic fuel. In low-temperature carbonisation, the amount of liquid products is relatively larger. The gas obtained as a by-product during low-temperature carbonisation has high calorific value of about 6500–9500 kcal/m³ and the yield is about 130–150 m³/ton of the coal carbonised. It is a valuable gaseous fuel.

The tar obtained as a by-product contains more of paraffinic hydrocarbons and small amount of aromatic hydrocarbons along with phenols and various other nitrogenated compounds.

There are two major commercial LTC plants in India. One is in Neyveli, Tamil Nadu, and the other is in Andhra Pradesh.

- (ii) **High temperature carbonisation** It is carried out at 900 °C–1200 °C and is used for the production of pure, hard, strong and porous metallurgical coke containing 1–3% volatile matter. The yield of coke is 65–75%.

The by-product gas and tar have greater amount of aromatic hydrocarbons. The yield of by-product gas is 370–480 m³/ton of coal carbonised but its calorific value is lower (5000–6000 kcal/m³) than that produced in LTC. The formation of lower amount of paraffins and higher amount of gas, indicates that cracking of paraffinic compounds present in coal takes place at high temperature, resulting in the formation of gases and greater aromatisation.

Table 1.3 Comparison between low and high-temperature carbonisation

S.No	Characteristic	Low-temperature carbonisation	High-temperature carbonisation
1	Carbonisation temperature	About 500–700 °C	900–1200 °C
2	Yield	75–80%	65–75%
3	Volatile matter content in coke	5–15%	1–3%
4	Mechanical strength of coke	Poor	Good
5	Hardness	Soft coke	Hard coke
6	Use of coke	For domestic purposes	For metallurgical purposes
7	Smoke produced on burning	Smokeless	Smoky
8	Yield of by-product gas	Lower (130–150 m ³ /ton of coal carbonised)	Higher (about 370–480 m ³ /ton of coal carbonised)
9	Calorific value of by-product gas	6500–9500 kcal/m ³	5000–6000 kcal/m ³
10	Percentage of straight chain hydrocarbon in by-products (tar and gas)	Higher	Lower
11	Percentage of aromatics in the by-products	Lower	Higher

Metallurgical coke

Coke is used as a heat source and reducing agent in metallurgy. Its properties depend on porosity, reactivity and the amount of volatile matter retained by coke during carbonisation. A good metallurgical coke should possess the following properties

- (i) **Purity** The moisture, ash, sulphur and phosphorus contents should be very low. Moisture reduces calorific value whereas excess of ash hinders the heating and also helps in slag formation. The presence of sulphur and phosphorus gives undesirable products like SO₂, P₂O₃ and P₂O₅ on burning, which adversely affect the quality of the metal being produced. The presence of sulphur makes the coke brittle.

- (ii) **Porosity** Coal should be porous so that oxygen can come in contact with carbon, which ensures efficient and complete combustion of the fuel in the furnace.
- (iii) **Strength** Coke should be compact, hard and strong enough to withstand high pressure in the furnace as well as to withstand the abrasive action of the ores, flux, etc.
- (iv) **Size** Metallurgical coke should be of medium size – neither too big nor too small. If the size is big, uniform heating is not possible, whereas small size of coke results in choking.
- (v) **Combustibility** Coke should burn easily but at the same time it should not be very reactive.
- (vi) **Calorific Value** The calorific value of coke should be high.
- (vii) **Cost** It should be cheap and easily available.
- (viii) **Calorific intensity** The calorific intensity of coke should be high enough to melt the metal.

Manufacture of metallurgical coke

Metallurgical coke can be manufactured by two methods:

- (i) Beehive oven method
- (ii) Otto Hofmann's oven or by-product oven or chamber oven method.

Beehive oven method

It is the earliest and cheapest method for the manufacture of metallurgical coke.

Construction It is a dome-shaped structure made up of bricks. It is about 4 m wide and 2.5 m high. It has two openings, one at the roof for charging the coal from the top and the other at the side for the entry of air and also for the removal of coke.

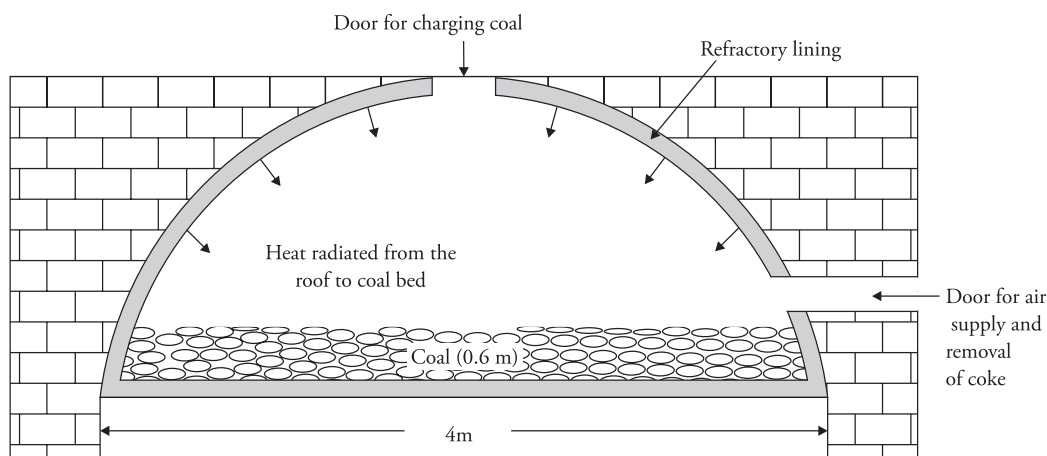


Figure 1.7 Beehive coke oven

Process The coal is introduced from the top hole of the dome and is spread evenly on the floor to give a layer of about 0.6–0.75 m thickness. The coal is ignited and just sufficient air is admitted

through the side opening to maintain the desired temperature. Carbonisation starts and the volatile matter burns inside the partially closed side door. Carbonisation proceeds from top to bottom and is completed in about 3 days. The oven is allowed to cool and the hard metallurgical coke formed is quenched with water and taken out through the discharge side door. The walls and roofs of the emptied oven are hot enough to start the carbonisation of the next batch. The yield of coke is about 60–80% and averages 5–6 ton coke per oven.

The process can be made more economical by operating a series of Beehive's ovens in such a way that hot gases escaping from one oven are utilised to ignite the charge in the adjacent oven.

Limitations of the process

- Coke yield low.
- Most volatile matter having many valuable by-products escapes into the atmosphere as waste.
- The exhaust gases cause pollution.
- Process is not flexible.

Otto Hofmann's oven or By-product oven or Chamber oven

Construction It consists of a number of narrow rectangular chambers made of silica bricks. Each chamber is 10–12 m long, 3–4 m high and 0.4–0.45 m wide. The chambers are tightly closed so that no air is admitted. At the top of each chamber, there are three holes for charging the coal. It is also provided with a gas take off (which carries out volatile matter) and discharging doors at the base for the removal of coke. These carbonisation chambers are erected side by side with interspaces for combustion of fuel gas. Thus, the ovens get heated from both sides. The ovens (chambers) form a sort of battery of 10–100 ovens. One single oven is capable of holding 16–24 tons of coal.

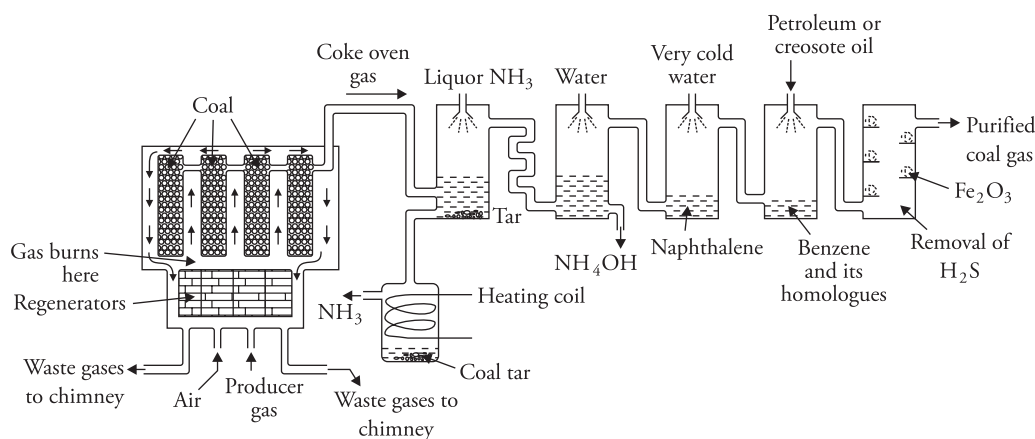


Figure 1.8 Otto Hofmann's coke oven method

Working

Finely crushed coal is introduced through the charging holes at the top of the chambers which are then closed tightly at both ends to cut off the supply of air. The ovens are heated to 1200 °C by burning gaseous fuels (such as producer gas). *Regenerative principle** of heat economy is employed to achieve as economical heating as possible.

The process of carbonisation starts in coal adjacent to the walls and moves towards the centre. As the coal is converted into coke, there is decrease in volume due to removal of volatile matter.

Carbonisation of a charge of coal takes about 11–18 h. After the process is complete, red hot coke is pushed out by means of a ram, which is electrically driven. The coke falls into a quenching car.

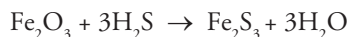
Quenching of red hot coke is carried out either by spraying water (wet quenching) or by passing inert gas such as N₂ from boilers (dry quenching). In wet quenching, sensible heat of coke is wasted, whereas in dry quenching the inert gases after quenching the coke become heated up and are circulated to the boilers where they generate steam. The coke produced by dry quenching is more strong, dense, graphitised and non-reactive. It is cheaper, dry and contains less dust than the wet quenched coke.

Recovery of by products

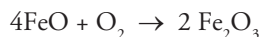
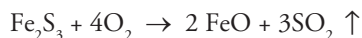
The gas coming out of the oven is known as ‘coke oven gas’ and is mainly composed of ammonia, H₂S, naphthalene, benzene, tar, moisture, etc. These are recovered as follows:

- (i) **Recovery of tar** The gases from the coke oven are passed through a tower in which liquor ammonia is sprayed. Tar and dust get collected in a tank below. The tank is provided with heating coils to recover NH₃. Ammonia is again sent to the top of the trickling tower and is used again.
- (ii) **Recovery of ammonia** The gases now enter another tower where water is sprayed. Ammonia goes into the solution as NH₄OH.
- (iii) **Recovery of naphthalene** The gases then pass to a cooling tower where water at low temperature is sprayed. Naphthalene gets condensed which is then collected.
- (iv) **Recovery of benzene** The gases then pass through a scrubber, where petroleum is sprinkled, resulting in the condensation of benzene and its homologues.
- (v) **Recovery of H₂S** The gases then enter a purifying chamber packed with moist Fe₂O₃. Here H₂S is retained.

*Regenerative principle is employed to achieve as economical heating as possible. In this the flue gases (waste gases produced after combustion) are passed through regenerators and then let off into the atmosphere through chimneys. Regenerators are built underneath the ovens. The flue gases pass their heat to the checker brick work of regenerators until the temperature rises to about 1000 °C. The flow of heating flue gases is then reversed and the inlet gas (fuel gas and air) used for combustion is passed through the heated checker brickwork of regenerators. Thus the inlet gases are preheated. After sometime again the flow of gases is reversed to heat the checker work. Hence the regenerator works on the principle of alternate heating and cooling cycles.



After sometime, when all Fe_2O_3 is changed to Fe_2S_3 , the purifier is exposed to atmospheric air, where Fe_2O_3 is regenerated.



- (vi) **Recovery of gas** The gas after passing through various condensers and scrubbers to remove the by-products mentioned above is finally collected in a gas holder. It is the coal gas whose calorific value is about 5000 kcal/m³.

1.9 Liquid Fuels

Liquid fuels are used extensively in industrial and domestic fields. Use of liquid fuels in internal combustion engines makes them very important fuels. The single largest source of liquid fuels is petroleum or crude oil (the term petroleum means rock oil. Latin-Petra means rock; oleum means oil) is a dark, greenish-brown viscous oil found deep inside the earth's crust. It is a mixture of hydrocarbons such as straight chain paraffins, cycloparaffins or naphthalene, olefins and aromatics along with small amount of organic compounds containing oxygen, nitrogen and sulphur.

Average composition of crude petroleum is

Element	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen
Percentage	75.5–87.1%	11.5–14.8%	0.1–3.5%	0.4–0.9%	0.1–0.9%

Classification of petroleum

Petroleum is classified into three categories according to its composition

1. **Paraffinic base petroleum** It is mainly composed of straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenes and aromatic hydrocarbons.
2. **Naphthenic or asphaltic base petroleum** It contains mainly cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons.
3. **Mixed base petroleum** It contains both paraffins and asphaltic hydrocarbons.

Table 1.4 Classification of Crude Petroleum

Type of petroleum	Constitution	Residue obtained after distillation	Remarks
Paraffinic base petroleum	Straight chain saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ along with small amounts of naphthenic and aromatic hydrocarbons	Solid paraffin wax	Furnish low octane number straight run gasoline

Naphthenic or asphaltic base petroleum	Cycloparaffins or naphthenes as main constituent along with smaller amount of paraffins and aromatic hydrocarbons	Asphalt or bitumen	Furnish high octane number straight run gasoline
Mixed base petroleum	Both paraffins and asphaltic hydrocarbons	Paraffin wax and asphalt	Furnish medium grade straight run gasoline

Mining of petroleum

Petroleum is found deep below the earth's crust. The oil is found to be floating over salt water or brine and has a layer of gas on top of it. Mining of oil is carried out by drilling holes in the earth's crust and sinking pipes up to the oil-bearing porous rocks. Oil rushes through these holes because of the pressure of natural gas. As the pressure of natural gas subsides, the oil is pumped out with the help of air lift pumps.

The air lift pump is a device containing two co-axial pipes lowered into the oil bed. The compressed air is forced through the outer pipe causing the oil to flow out through the inner pipe. This oil is then led to the refinery and processed.

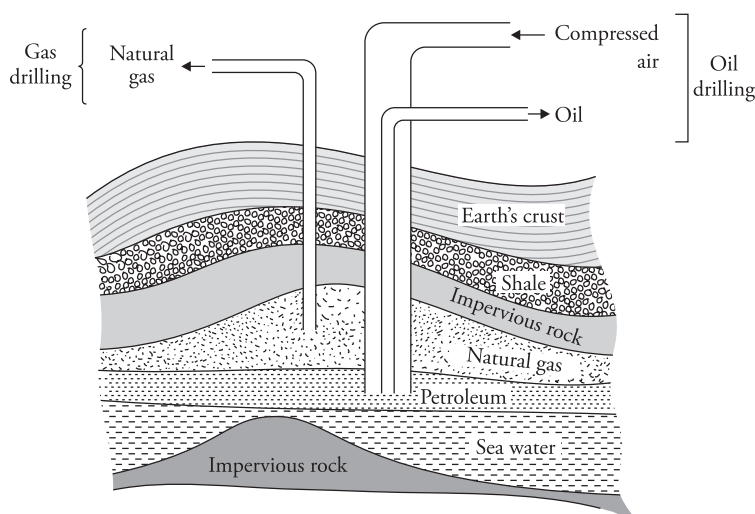


Figure 1.9 Mining of petroleum

1.10 Refining of Petroleum

Crude oil coming out from the oil well is a mixture of solid, liquid and gaseous hydrocarbons containing sand and water in suspension. After removal of dirt, water, sulphur and other impurities, this oil is subjected to fractional distillation. This process of removing unwanted impurities and separating petroleum into useful fractions with different boiling ranges is called *refining of petroleum*. The process of refining involves the following steps.

1. **Separation of water (demulsification)** The crude oil from the well is an extremely stable emulsion of oil and salt water. The demulsification is achieved by *Cotrell's process*. The crude oil is allowed to flow between two highly charged electrodes where colloidal water droplets coalesce to form large drops which separate out from the oil.
2. **Removal of harmful impurities** NaCl and MgCl_2 corrode the refining equipments. These are removed by modern techniques like electrical desalting and dehydration.

Harmful sulphur compounds are removed by treating the crude oil with copper oxide. Sulphur reacts with copper oxide forming copper sulphide, which is removed by filtration.

3. **Fractional distillation** The crude oil is heated to 400°C in an iron retort whereby all the volatile constituents, except asphalt or coke are evaporated. The vapours are then passed into a fractionating column, which is a tall cylindrical tower. The tower is hot towards the lower end and comparatively cooler at the upper end. It consists of a number of horizontal stainless steel trays at short distances. These trays are provided with individual chimneys which are covered with a loose cap. As the vapours go up, fractional condensation occurs at different heights of the column. Higher boiling fractions condense first, while lower boiling fractions condense later as shown in Figure 1.10.

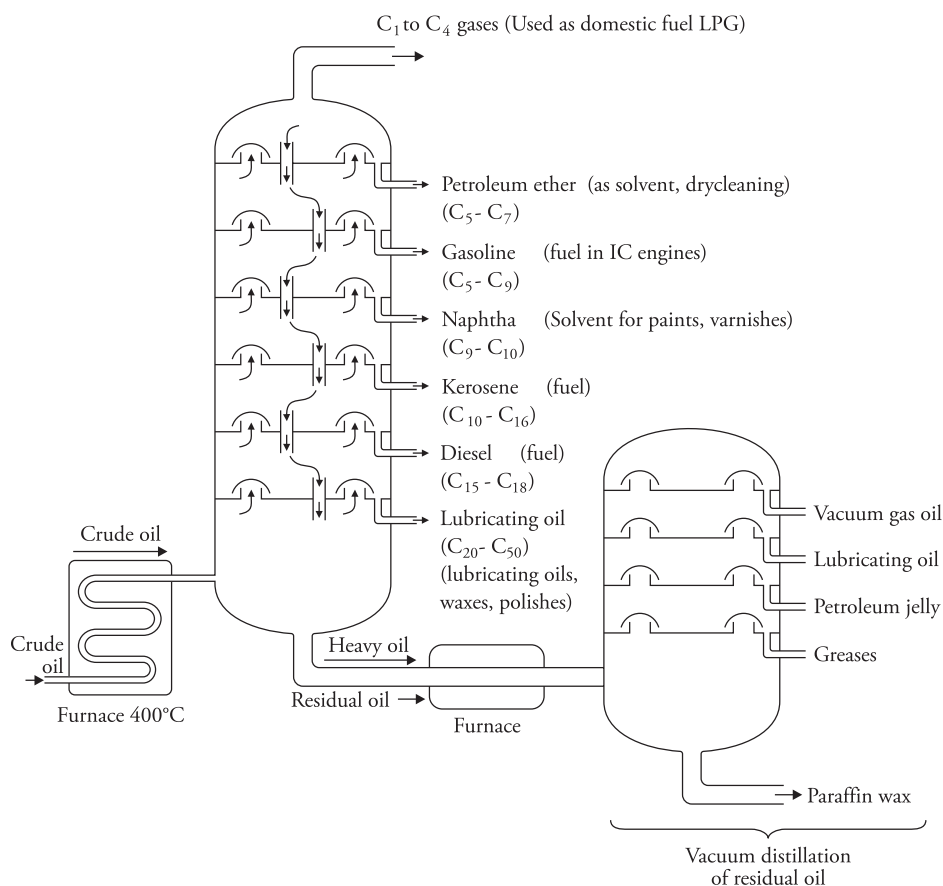


Figure 1.10 Fractional distillation of crude oil

The residue from the bottom of fractionating tower is vacuum-distilled to recover various fractions.

The names, approximate composition, range and uses of various fractions are given below in Table 1.5.

Table 1.5 Major fractions obtained by the distillation of crude oil

S.No.	Fraction's name	Boiling temperature	Approximate composition in terms of hydrocarbons containing C atoms	Uses
1	Uncondensed gases	Below 30 °C	C ₁ –C ₄	Used as domestic fuel (LPG)
2	Petroleum ether	30–70 °C	C ₅ –C ₇	Solvent for fats, essential oils, used in dry cleaning
3	Gasoline or petrol or motor spirit	70–120 °C	C ₅ –C ₉	As a motor fuel for IC engines, as a solvent and in dry cleaning
4	Naphtha or solvent spirit	120–180 °C	C ₉ –C ₁₀	As a solvent for paints and varnishes and in dry cleaning
5	Kerosene oil	180–250 °C	C ₁₀ –C ₁₆	Fuel for stoves, jet engine fuel and for preparing oil gas used in laboratories
6	Diesel oil	250–320 °C	C ₁₅ –C ₁₈	Diesel engine fuel
7	Heavy oil Heavy oil on vacuum distillation gives i. Lubricating oil ii. Petroleum jelly (vaseline) iii. Greases iv. Paraffin wax	320–400 °C – – – –	C ₁₇ –C ₃₀ C ₁₇ –C ₂₀ – C ₂₀ –C ₂₈	Fuel for ships, in metallurgical furnaces and in conversion to gasoline by cracking As lubricants Used in cosmetics and medicines In candles, boot polishes, wax paper, etc.
8	Residue: It may be either i. Asphalt (if the crude oil is asphaltic) ii. Petroleum coke	> 400 °C	C ₃₀ and above	Used for water proofing of roofs and for road making As a fuel in moulding electrode rods for cells

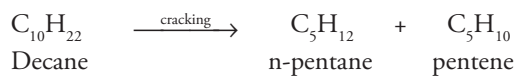
The gasoline obtained by this fractionation is called *straight run gasoline*.

1.11 Cracking

The crude oil obtained on fractionation yields approximately 20–30% gasoline, 30–35% middle oils and 20–25% heavy oils. Among all these fractions, gasoline (also called straight run petrol) is in maximum demand because of its use as fuel in the automobile industry. Hence, there is a need to

convert the middle oil and heavy oil fractions into a more useful fraction gasoline. This is achieved by *cracking*.

Cracking is defined as the process of converting high-molecular-weight bigger hydrocarbons into low-molecular-weight smaller hydrocarbons by the application of heat, with or without a catalyst.



Nearly 50% of today's gasoline is obtained by cracking. It is important to note that the characteristics of gasoline obtained by cracking are far more superior to the straight run gasoline. The methods of cracking are summarised below

1. **Thermal cracking** When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking. The bigger hydrocarbons breakdown to give smaller molecules of paraffins, olefins and some hydrogen. This process may be carried out either in liquid phase or in vapour phase.
 - (a) **Liquid phase thermal cracking** By this method any type of oil (residue, fuel oil or gasoline) can be cracked. The charge is kept in liquid form by applying high pressure of the range of 100 kg/cm² at a suitable temperature of 475–530 °C. The cracked products are separated in a fractionating column. The octane rating of the product is 65–70.
 - (b) **Vapour phase thermal cracking** This method is suitable for oils which can be readily vapourised. The oil is first vaporised and then cracked at about 600–650 °C and under a low pressure of 10–20 kg/cm². It requires less time than the liquid phase method. Petrol obtained from vapour phase cracking has better antiknock properties, but poorer stability than the petrol obtained from liquid-phase cracking.

Table 1.6 Comparison of liquid phase and vapour phase thermal cracking

Characteristic	Liquid phase thermal cracking	Vapour phase thermal cracking
Cracking temperature	475 – 530 °C	600–650 °C
Pressure	100 kg/cm ²	10–20 kg/cm ²
Octane rating of petrol	65–70	Greater than 70
Type of oil used for cracking	Any heavy oil can be cracked	Oil should be readily vapourised

2. **Catalytic cracking** It is carried out in the presence of a catalyst at a much lower temperature and pressure. The catalyst used is usually a mixture of silica and alumina (hydrated aluminium silicate) or zeolites in the form of beads or pellets.

There are two main types of catalytic cracking.

- (a) **Fixed bed catalytic cracking** The vapours of the oil are preheated in a pre-heater to a temperature of 420–450 °C. It is then passed through a catalytic chamber containing

either silica-alumina gel (SiO_2 , Al_2O_3) or bauxite mixed with clay and zirconium oxide maintained at $425\text{ }^\circ\text{C}$ – $450\text{ }^\circ\text{C}$ and 1.5 kg/cm^2 pressure. Cracking of heavy oil vapours takes place and 30–40% of the charge is converted into gasoline and about 3–4% carbon is formed which gets adsorbed on the catalyst bed. The cracked vapours then pass through a cooler where some gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabiliser’ where the dissolved gases are removed and pure gasoline is obtained.

After 8–10 h, the catalyst stops functioning because of the deposition of black layer of carbon formed during cracking. This is re-activated by burning off the deposited carbon. During the reactivation of the catalyst, the vapors of heavy oil are diverted through another standby catalytic chamber so that the reaction proceeds continuously.

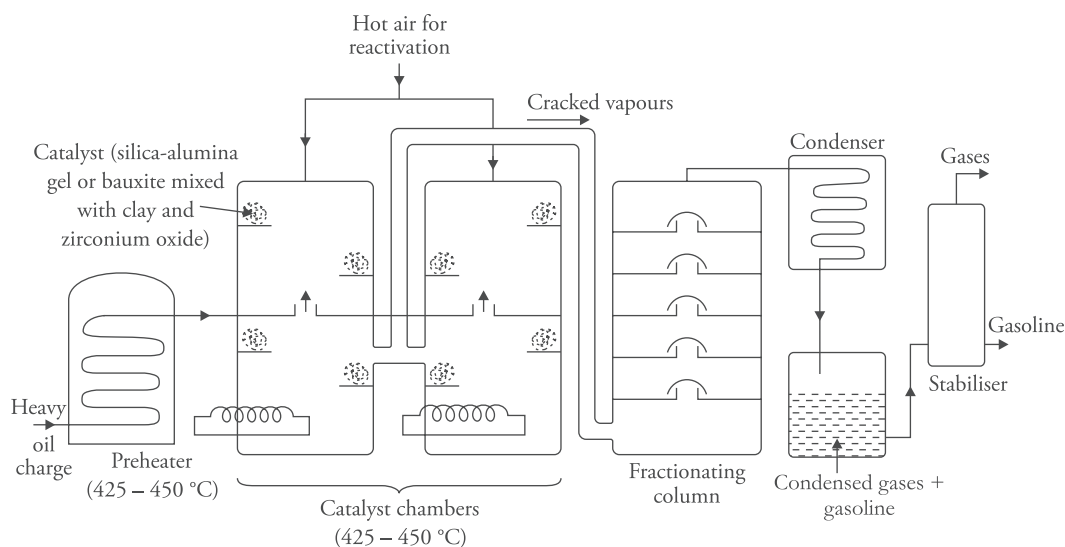


Figure 1.11 Fixed bed catalytic cracking

- (b) **Moving bed catalytic cracking** This is also known as fluidised bed catalytic cracking. The feed oil is preheated. It is then mixed with powdered catalyst and the mixture of preheated heavy oil and powdered catalyst goes in a reactor maintained at $500\text{ }^\circ\text{C}$. Cracking of heavy oil takes place. Near the top of the reactor there is a centrifugal separator (called cyclone) which allows the cracked vapours to pass on to the fractionating column but retains the catalyst powder. The catalyst powder gradually becomes heavier, due to coating with carbon formed and settles at the bottom. This is called *spent catalyst* and is forced by a blast of air to the regenerator maintained at $600\text{ }^\circ\text{C}$. In regenerator, carbon is burnt off and the catalyst is reactivated. The regenerated catalyst then flows through a standpipe to get mixed with fresh charge. The cyclone at the top of the regenerator allows the flue gases (e.g., CO_2) to escape retaining the catalyst particles.

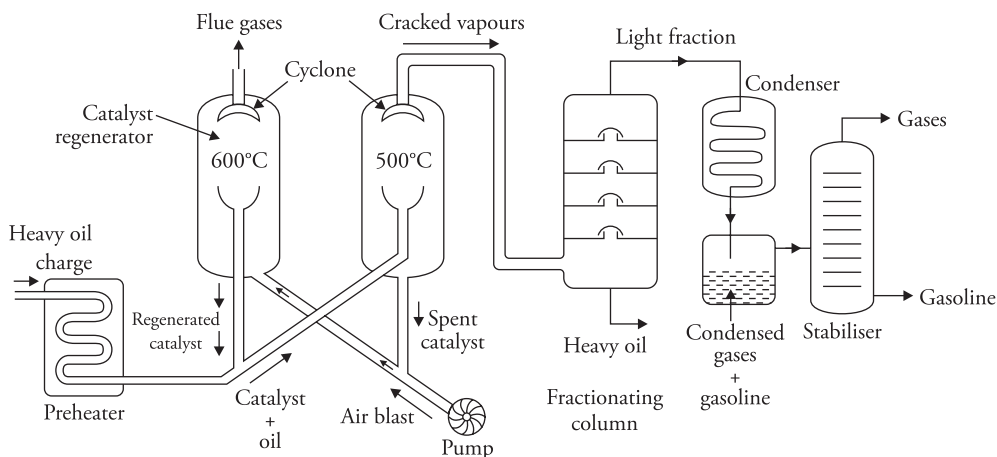


Figure 1.12 Moving bed type catalytic cracking

Advantages of catalytic cracking over thermal cracking

1. The yield of gasoline is higher. About 70% of the raw material by weight is converted into gasoline. The yield of gaseous products (by-product gases such as alkanes and alkenes) is about 12–15% and only 4–6% of the raw material is converted into coke.
2. Production cost is low as high temperatures and pressures are not needed (pressure 1–5 kg/cm²).
3. No external fuel is required for cracking since the heat required is obtained by burning the carbon deposited on the catalyst itself during regeneration process.
4. Process can be controlled to obtain desired products.
5. The percentage of gum or gum-forming compounds is very low.
6. The process is faster.
7. Action of catalysts is selective, hence cracking of only high-boiling hydrocarbons takes place.
8. The quality of gasoline produced is better because
 - (i) The product contains very little amount of undesirable sulphur as the major portion of it escapes out as H₂S during cracking.
 - (ii) The gasoline obtained by cracking contains low percentage of olefins and higher percentage of isoparaffin and aromatic hydrocarbons. This increases the antiknock properties of gasoline. Gasoline formed by catalytic cracking has an octane number of 80.

Decomposition of aromatics removes only side chains but the aromatic ring is not broken.

1.12 Synthetic Petrol

Petrol can be synthesised by the following methods.

1. **Polymerisation** In this method small molecules of hydrocarbons are combined to form heavier molecules resembling gasoline.

During cracking large quantities of olefins or unsaturated hydrocarbons (such as ethylene, propene and butene) and alkanes (such as methane, ethane, and butane) are obtained as by-products. When this gaseous mixture is subjected to high pressure and temperature, with or without a catalyst, it polymerises to form higher hydrocarbons resembling gasoline.

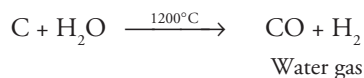
The gasoline so obtained is called polymer gasoline. It has high octane number (78 to 83). Polymerisation is carried out in two ways.

- (i) **Thermal polymerisation** In this the polymerisation of cracked gases is carried out at 500–600 °C and 70–350 kg/cm² pressure. The product is gasoline and gas-oil mixture which are separated by fractional distillation.
 - (ii) **Catalytic polymerisation** It is carried out in the presence of catalyst like phosphoric acid, sulphuric acid, etc. The process is carried out at a low temperature (150–200 °C)
2. **Alkylation** This method is used to convert olefins to gasoline. In this process, alkane and alkene are combined together in the presence of a catalyst under proper temperature and pressure. The most important example is the reaction of isobutane and isobutene in the presence of anhydrous HF at room temperature to give isooctane. This process is used to produce gasoline of improved quality.

Conversion of coal into liquid fuels

Coal can be converted into gasoline by two methods:

- (a) **Fischer Tropsch method** This method was developed by Fischer and Tropsch in 1962 in Germany. It is an indirect method of converting coal into liquid fuel, where the raw material is coke, which is converted into water gas (CO + H₂) by passing steam over red-hot coke.

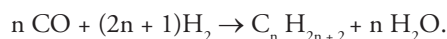
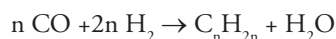


A mixture of water gas and hydrogen is purified by passing through Fe₂O₃ (to remove H₂S) and then through a mixture of Fe₂O₃ + Na₂CO₃ (to remove organic sulphur compounds).

The purified gas is compressed to 5–25 atm and then passed through a catalytic converter maintained at about 200–300 °C. The catalyst consists of a mixture of

Cobalt (100 parts), Thoria (5 parts), Magnesia (8 parts) and Keiselguhr earth (200 parts)

A mixture of saturated and unsaturated hydrocarbons is formed.



The reactions leading to the formation of hydrocarbons are all exothermic. The vapors coming out of the reaction chamber are passed through the cooler where liquid resembling

crude oil is obtained. This is then subjected to fractional distillation to yield gasoline, diesel oil and heavy oil. The heavy oil can be reused for cracking to obtain more gasoline.

The gasoline formed by Fischer Tropsch process is rich in straight chain hydrocarbons, and hence its octane number is only 40. However, the diesel oil obtained is of excellent quality.

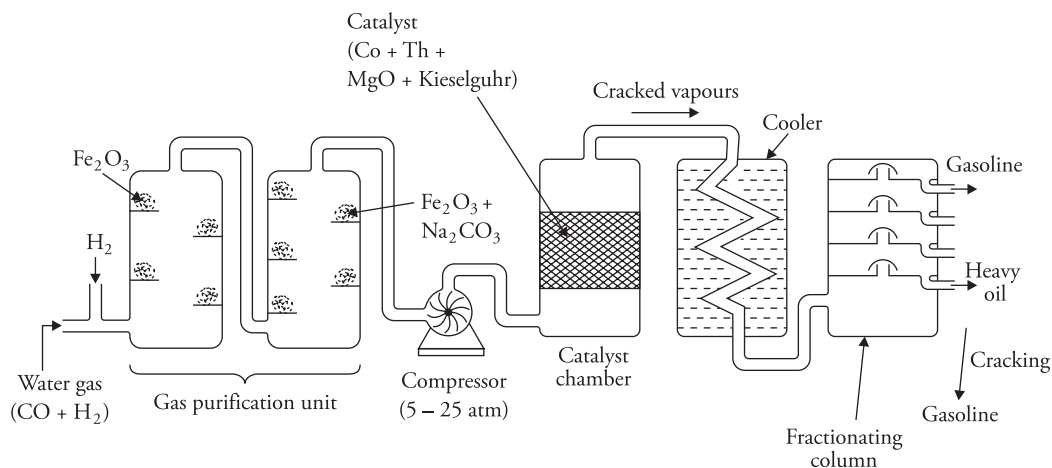


Figure 1.13 *Fischer - Tropsch method*

(b) **Bergius process**

This is the direct method of converting coal into gasoline (liquid fuel). This process developed by Bergius of Germany involves the conversion of low-grade coals, such as bituminous coals or brown coals, into liquid and gaseous fuels by hydrogenating them in the presence of catalyst.

In this process, the low ash coal is powdered and mixed with heavy oil and catalyst (tin and Ni oleate) to make a paste. This paste is heated with hydrogen at 450 °C and 200–250 atm pressure for about 2 h. The coal undergoes hydrogenation to form saturated hydrocarbons that decompose at prevailing high temperature and pressure to yield low-boiling liquid hydrocarbons. The vapors leaving the catalytic chamber are condensed, where a liquid resembling crude oil is obtained. This is subjected to fractional distillation to give (i) gasoline, (ii) middle oil and (iii) heavy oil.

The middle oil is again hydrogenated to obtain gasoline. Heavy oil is reused for making a paste with fresh coal dust.

The gasoline so obtained contains 74% paraffins, 22% aromatics and 4% olefins. The yield of gasoline is about 60% of the coal dust used.

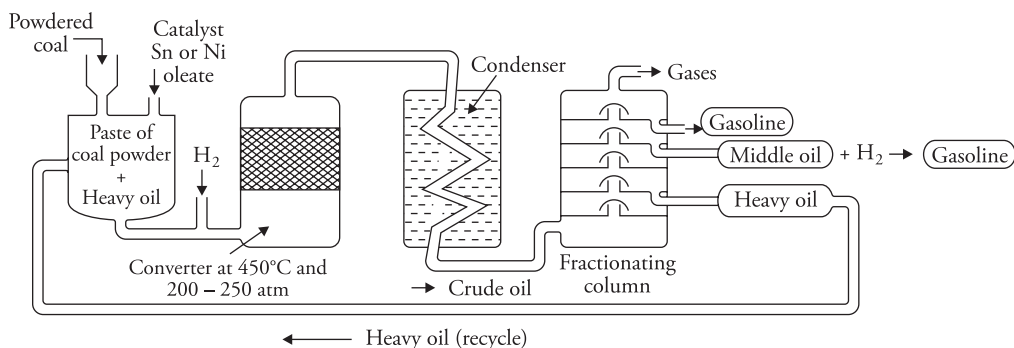


Figure 1.14 Bergius process of hydrogenation of coal to gasoline

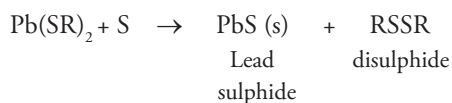
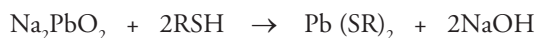
Refining of gasoline

The straight run gasoline obtained from fractionation of crude petroleum or by synthesis contains substances such as (i) unsaturated olefins and (ii) sulphur. These substances are undesirable because

- Olefins undergo oxidation and polymerisation leading to gum and sludge formation. These deposit on the walls of the carburetor and stop the engine.
- The sulphur compounds lead to corrosion of internal combustion engine. Moreover, compounds of sulphur such as mercaptans or H_2S have objectionable odors and make the oil sour.

Hence it has to be refined by chemical treatment.

- (a) **Removal of sulphur compounds** The sulphur-containing gasoline is termed as sour gasoline and the process of removal of sulphur is called 'sweetening'. It is accomplished by treating gasoline with sodium plumbite with controlled addition of sulphur. The sulphur compounds are converted into PbS (removed by filtration) and disulphides (which are extracted with a suitable solvent). The above process is termed as **Doctors process**.



- (b) **Removal of olefins** They are removed by percolating gasoline through Fuller's earth, which preferentially adsorbs colours and olefins.
- (c) **Stabilisation of gasoline** Impure gasoline may contain dissolved gases such as methane, ethane, propane and butane. The process of removal of these impurities is called stabilisation. For this, impure gasoline is passed through a fractionating tower having plates. The lower plates are heated with steam and are introduced near the upper plates. The stabilised gasoline is removed from the top of the column.

- (d) **Blending** Purified gasoline is blended with high octane number fractions.
- (e) **Addition of inhibitors** After refining, some inhibitors such as aromatic amines and aminophenols are added. These retard the oxidation process and prevent gum formation during storage.
- (f) **Doping** In order to improve the antiknocking properties, tetraethyllead (TEL) is added. This is called doping.

Characteristics of ideal gasoline

1. It must be cheap and readily available.
2. It must have a high calorific value.
3. It should be stable in storage. It should not form solid or gummy products on standing.
4. On combustion it should not cause corrosion in the engine. It should be free from water, sulphur compounds and other corrosion producing constituents.
5. It must be knock resistant and should have high octane number.
6. It should burn clean and should leave little carbon deposit during combustion.
7. It should have proper and partial vaporisation on mixing with air in internal combustion engines. If it does not vaporise there will be difficulty in starting the engine. On the other hand if the volatility of gasoline is too high, it leads to vapour formation in the fuel line causing vapour locking. This reduces the fuel supply and the engine stops.
8. It should not pre-ignite easily.
9. It should not tend to decrease the volumetric efficiency of the engine.
10. It should have a high specific gravity where there is a space limitation such as in aviation applications.

1.13 Knocking

It is defined as the metallic sound similar to rattling of hammer produced in internal combustion engine due to immature ignition of fuel air mixture.

An internal combustion engine uses either gasoline or diesel as fuel. In internal combustion engine, a mixture of fuel (gasoline or diesel) is ignited in a cylinder. The ignition is brought about by means of an electric spark (in petrol engines) or by compressing the air (in diesel engines).

The gases evolved during ignition, force the piston down due to high pressure thus producing the power stroke.

In a petrol engine the whole process comprises of four strokes;

- (i) **Suction stroke** The downward moving piston sucks a mixture of air and petrol vapours in the carburetor into the cylinder.
- (ii) **Compression stroke** The piston moves up, compressing the gas mixture. The ratio of initial volume (volume at suction stroke) to final volume (volume at compression stroke) is called compression ratio. It is here that a low octane rating fuel might ignite and cause knocking.

- (iii) **Power stroke** Just before the piston reaches the top centre of the cylinder a spark from the spark plug ignites the gas mixture. The hot gases produced due to combustion increase the pressure and push the piston down.
- (iv) **Exhaust stroke** This is the last stroke in which the piston rises up and expels the exhaust gases from the cylinder.

The cycle then repeats itself. After the reaction is initiated by a spark, the fuel air mixture should burn smoothly and rapidly so that the expanding gas drives the piston down the cylinder smoothly.

Figure 1.15 represents schematic diagram of a four-stroke spark-ignition engine.

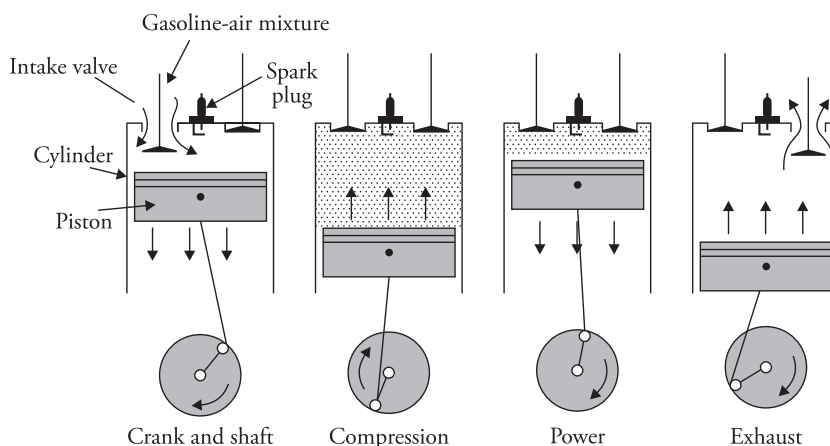


Figure 1.15 Schematic diagram of a four-stroke, spark-ignition engine

The efficiency of internal combustion engine depends on the compression ratio. Higher the compression ratio greater is the efficiency of the engine. To achieve maximum efficiency, a compression ratio of about 7–8 is required. However, if the compression ratio exceeds a certain limit, the fuel–air mixture may get heated to a temperature greater than its ignition temperature and spontaneous combustion of the fuel occurs even before sparking. This is called **pre-ignition**. As a result of pre-ignition, the unburned fuel air mixture gets heated to such an extent that some of the hydrocarbons reach their ignition temperature and ignite all at once – explosively causing a metallic sound called **knocking**.

Knocking decreases the efficiency of the engine and causes huge loss of energy and damage to piston and cylinder. Knocking depends on the chemical composition of the fuel, engine design, shape of head, location of plug, ports, etc., and also upon the running conditions.

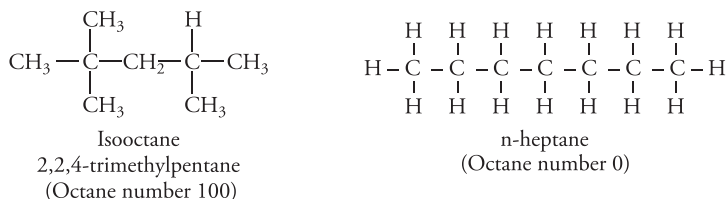
Chemical structure and knocking

1. The knocking tendency decreases with increase in compactness of the molecule.
2. Knocking decreases with the increase in the number of double bonds and rings (cyclic structure).
3. With normal paraffins, the knocking increases with increase in length of the hydrocarbon chain. Thus, the knocking tendency increases from n-butane to n-heptane.

- n-butane < n-pentane < n-hexane < n-heptane
 ————— knocking increases —————>
4. Knocking decreases as the branching in carbon chain increases.
 n-heptane > 2-methylhexane > 2, 2-dimethylpentane
 ————— knocking decreases —————>
5. Aromatics such as benzene and toluene have very high antiknock properties.
 In general the tendency of fuel constituents to knock is in the following order
 Straight chain paraffins > branched chain paraffins (i.e., isoparaffins) olefins > cycloparaffins
 (i.e., naphthalenes) > aromatics.

1.14 Octane Rating

In order to classify the fuels according to their knocking property, an arbitrary scale was provided by Edger in 1926, known as octane rating or octane number. It is observed that n-heptane knocks very badly; hence, it was arbitrarily assigned an antiknock value of zero. On the other hand, isooctane (2,2,4-trimethylpentane) has a high resistance to knocking and hence was arbitrarily assigned a value of 100.



Octane number of a fuel is defined as the percentage of isooctane in a mixture of isooctane and n-heptane, which has the same knocking characteristics as that of the fuel under examination, under same set of conditions. Thus, a fuel with octane number 80 is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.

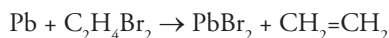
Antiknocking agents Octane number of gasoline can be increased by addition of additives like benzol and alcohol. This process is called ‘blending’.

The antiknock properties of gasoline are usually increased by adding tetraethyl lead (TEL) $\text{Pb}(\text{C}_2\text{H}_5)_4$ and the process is called ‘doping’. TEL is a colourless liquid with a sweet odour but it is highly poisonous. About 0.5 mL of TEL per liter is added for motor fuels and about 1 mL of TEL per liter is added for aviation fuel. Gasoline containing TEL is coloured with 2% red dye to indicate its poisonous nature.

It is believed that knocking is a free radical mechanism. During combustion $\text{Pb}(\text{C}_2\text{H}_5)_4$ forms Pb and PbO. These act as free radical chain inhibitors and hence the propagation of the chain reaction leading to knocking does not take place.

However lead and lead oxide vapours so formed contaminate the atmosphere. Lead oxide is rapidly reduced to metallic lead which is deposited on the spark plug, cylinder walls and piston head. Hence, it is harmful to the engine. In order to solve these problems ethylene dibromide

(C₂H₄Br₂) is also added, so that lead formed is converted into lead bromide, which is volatile and escapes into the atmosphere.



Owing to harmful effects of lead, these days *unleaded petrol* is being used.

Unleaded petrol It is one where octane number is increased without the addition of lead compounds. High octane number compounds such as isopentane, isooctane, ethylbenzene, isopropyl benzene, methyl tertiary butyl ether (MTBE) are used. Out of these, MTBE is preferred because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing peroxy compound formation.

Use of unleaded petrol requires the use of catalytic converter. A catalytic converter contains a catalyst (rhodium), which converts the toxic gases (CO and NO) to harmless gases (CO₂ and N₂, respectively). Moreover, it oxidises unburnt hydrocarbon into CO₂ and H₂O.

1.15 Diesel Engine Fuels

In a diesel engine, the fuel is ignited not by a spark (as in petrol engine), but by the application of heat and pressure. The combustion cycle has four strokes

- (i) **Suction stroke** In this the air is drawn into the cylinder.
- (ii) **Compression stroke** Here, the air is compressed to a pressure of 30–50 kg/cm². Compression leads to rise in temperature to about 500 °C.
- (iii) **Power stroke** Towards the end of compression stroke, that is, when the piston reaches its top centre (top centre is the moment when the piston has travelled into the cylinder as far as it can go and the compression is at its maximum), the diesel oil is injected in the form of fine droplets into the very hot compressed air. The fine particles of fuel absorb heat from the compressed air (at about 500 °C) and ignite. The pressure of the gases evolved during the ignition/combustion pushes the piston downwards.
- (iv) **Exhaust stroke** This is the last stage of the cycle. In this the expulsion of hot gases from the cylinder takes place.

1.16 Knocking in Diesel Engine

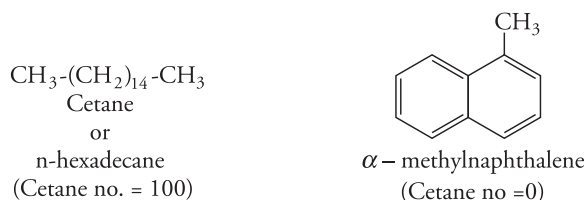
Ideally, ignition in diesel engine should begin just as the piston reaches the top center. When this does not happen, there occurs a time lag between injection of fuel and its ignition. *This interval between the start of fuel injection and its ignition is termed as ignition delay or induction delay.* It is obvious that for the efficient functioning of the diesel engine, this induction lag should be as brief as possible.

When a fuel has long induction lag a portion of the injected fuel gets accumulated in the cylinder even before ignition and when ignition takes place, the accumulated fuel burns violently leading to sudden increase in temperature and pressure. This non-uniform burning of the fuel is known as *diesel knocking*. The greater is the induction lag, higher is the diesel knock.

Chemically, diesel engine fuels consist of straight chain hydrocarbons with minimum amount of branched chain and aromatic hydrocarbons. Thus, in contrast to gasoline, the diesel engine fuel should have low spontaneous ignition temperature so as to minimise the induction lag.

1.17 Cetane Rating/Cetane Number

Cetane number is a measure of ignition quality of a diesel fuel. It is often mistaken as a measure of the fuel quality. It is actually a measure of the fuel's ignition delay. It is the measure of the ease with which the fuel will ignite under compression. The hydrocarbon cetane (n-hexadecane) has a very short ignition delay as compared to any diesel fuel and is assigned an arbitrary value of 100. α -methyl naphthalene has a long ignition delay compared to any other diesel fuel and hence is assigned a value of 0 (zero).



The cetane number of a diesel fuel is defined as the percentage of cetane (n-hexadecane) in a mixture of cetane and α -methylnaphthalene, which will have the same ignition characteristics as the fuel under test, under the same conditions. For example, a diesel fuel will be assigned a cetane number of 60 if it has the same ignition characteristics as that of a mixture of 60% cetane (n-hexadecane) and 40% α -methylnaphthalene. The cetane value of a fuel depends upon the nature and composition of hydrocarbon. The straight chain hydrocarbons ignite quite readily, although aromatics do not ignite easily. Ignition quality order among the constituents of diesel engine fuels in order of decreasing cetane number is as follows:

n-alkanes > naphthalene > alkenes > branched alkanes > aromatics

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

The cetane number of a diesel fuel can be raised by addition of small quantity of certain 'pre-ignition dopes' such as ethylnitrite, isoamyl nitrite, acetone peroxide, etc.

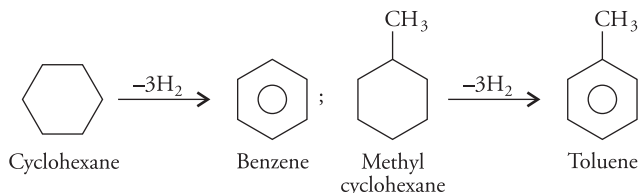
High-speed and Low speed diesel In a high-speed diesel engine the time lag in getting the diesel droplets heated to ignition point is very small, about $1/500^{\text{th}}$ of a second. Such diesel engines require diesel with cetane number in excess of 45 (up to 60). On the other hand, low speed diesel requires a cetane number of about 25. The cetane number of medium speed diesel is about 35.

1.18 Reforming

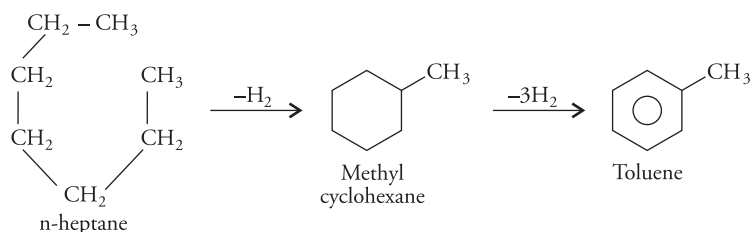
Reforming is the process of improving the antiknocking characteristics of gasoline by bringing about certain structural modifications in it. The modifications are due to the rearrangement of

molecules without disturbing their average molecular weight. The main reactions involved in reforming process are

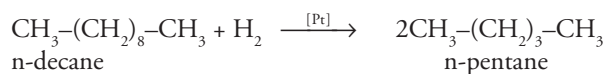
(i) **Dehydrogenation** (removal of hydrogen)



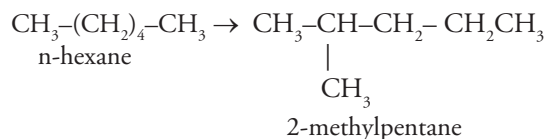
(ii) **Dehydrocyclisation** (removal of hydrogen followed by cyclisation)



Hydrocracking (breaking of the molecule in presence of H₂)



Isomerisation



Reforming can be carried out either thermally or in the presence of a catalyst.

Thermal Reforming In this process, the straight run gasolines are heated to a temperature of 500–600 °C at a pressure of about 85 kg/cm². The degree of reforming is controlled by rapid cooling (quenching) with an oil spray. The reformed products are fractionated to remove residual gases. Alkanes and alkenes formed due to cracking may undergo dehydrogenation and cyclisation to form naphthalenes. n-alkanes may also get converted into branched chain hydrocarbons (isomerisation).

Catalytic reforming Catalytic reforming is carried out in the presence of a catalyst (platinum supported on alumina). It is carried out at 460–530 °C and a pressure of 35–51 kg/cm². It can be either fixed bed or fluidised bed.

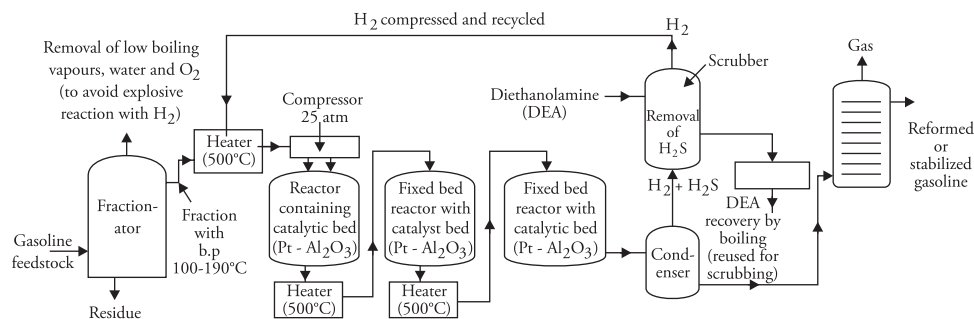


Figure 1.16 Catalytic reforming

Water, low boiling vapours, and oxygen are removed from the feedstock by heating and fractionation. This is done to avoid any explosive reaction with hydrogen. Out of different fractions obtained by fractionation, the fraction with boiling point 100–190 °C is selected and mixed with compressed hydrogen. This mixture is heated upto 500 °C by passing through a heater and is then compressed to 25 atm. The mixture is then passed through a series of three reactors, each containing Pt-Al₂O₃ catalyst bed.

As reforming is an endothermic process, hence the vapours have to be preheated before passing them from one reactor to the other. The products are condensed and separated into liquid and gaseous phase (consisting of H₂ and H₂S). H₂S is derived from sulphur compounds present in gasoline. It is removed by absorbing it in diethanolamine (DEA) in an H₂S scrubber. Part of H₂ formed is recycled for removing S in feedstock as H₂S and remaining is used for other purposes like hydrogenation of alkenes and hydrocracking. DEA can be regenerated by boiling and can be reused for scrubbing. The residue from the condenser is fractionated to remove the gases and higher boiling fractions.

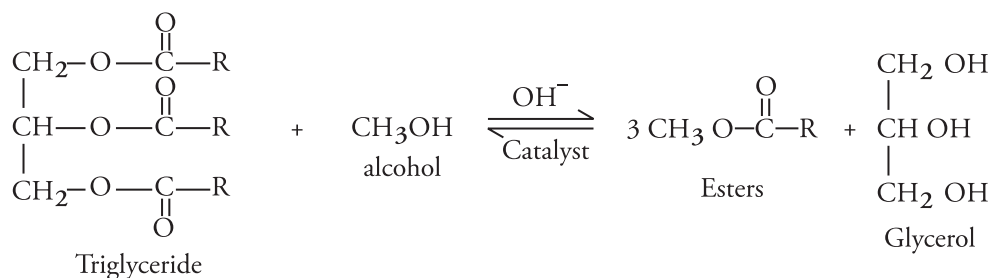
1.19 Non Petroleum Fuels, Power Alcohol and Aviation Fuel

- (a) **Benzol** It contains 70% benzene, 18% toluene and 6% xylene and rest other hydrocarbons and is obtained during the fractional distillation of light oil in the temperature range 80–170 °C. Calorific value is 10200 kcal/kg and has an octane value of 87–90. It serves as a good fuel for internal combustion engines but cannot be used in cold countries as its freezing point is 55 °C. It is generally used as a blending agent with gasoline.
- (b) **Power alcohol** Power alcohol is a mixture of 5–25% ethyl alcohol with petrol and is used as a fuel in the internal combustion engines. Ethyl alcohol with an octane number of about 111 has good antiknocking properties, whereas the octane number of most commercial grade gasoline used in vehicles ranges from 87 to 94. Thus, blending petrol with ethyl alcohol improves the antiknocking properties and octane number of the former and reduces carbon monoxide emissions from the engine. On storage some gasolines form gums due to oligomerisation of alkenes and alkadienes. Gum formation is reduced in gasoline-alcohol blends due to the absence of alkenes or alkadienes in ethanol.

In spite of all these advantages use of ethyl alcohol is not very common because

- Its calorific value (7000 kcal/kg) is much lesser than the calorific value of petrol (11500 kcal/kg). Hence, addition of ethyl alcohol to petrol reduces its calorific value by 35%.
- Its surface tension is high and it is difficult to atomise it at lower temperature. This leads to starting trouble in a vehicle and the vehicle remains sluggish for quite some time after starting.
- Ethyl alcohol oxidises into acid, causing corrosion of the engine parts.

- (c) **Biodiesel** Biodiesel is produced by the base catalysed transesterification of vegetable oils such as soyabean oil, palm oil, sunflower oil, rapeseed oil, cotton oil, jojoba, jatropha and castor oil. The triglycerides present in these oils on reaction with excess alcohol (methanol or ethanol) in the presence of catalysts yield monomethylesters or monoethyl esters of long chain fatty acids and glycerol. Methanol is preferred over ethanol as its use in biodiesel production requires simpler technology. The following reaction is involved:



Excess alcohol is used to ensure complete conversion of triglyceride into products. The mixture is allowed to settle so that glycerol being heavy settles down at the bottom and is separated by gravity separation method.

Both the products glycerol and biodiesel have excess methanol, which has to be separated. It is removed either by distillation or by flash evaporation. The biodiesel thus obtained is purified to remove the catalysts, dried and stored. In some cases biodiesel is distilled to remove the coloring agents. Biodiesel can be used as a fuel in a conventional diesel engine without any modification. It has low toxicity, does not emit out sulphurdioxide and has a higher flash point as compared to the fossil diesel. However as compared to conventional diesel its shelf life is less (not more than six months) and it degrades rapidly. It has lower calorific value and hence its consumption is higher than normal diesel.

- (d) **Aviation fuels** The fuels used in spacecraft and aircrafts should be compact, light weight, occupy less space and produce more energy.

Aircrafts use special type of petroleum-based fuels, which are of a higher quality than those used in road transport. The fuels are blended with thousands of chemicals such as antioxidants and flame retardants that improve their performance and reduce the risk of explosion because of high temperature.

The fuels used in rocket help in their propulsion. They are combustible substances that burn to produce hot gases that eject out at a nozzle and help to propel the rocket or spacecraft in the forward direction. The fuels used consist of a substance that burns (fuels), a substance

that assists burning (an oxidiser), certain metallic additives and performance improvers. The propellants used can be solid propellants, liquid propellants or hybrid propellants.

In solid propellants, the fuel is generally hydroxy-terminated polybutadiene (HTPB). Any one of the following oxidisers such as ammonium perchlorate, potassium perchlorate, ammonium nitrate, potassium nitrate or even cyclotrimethylene trinitramine (RDX) can be used. Powders of certain metals such as aluminium, magnesium and beryllium are also added. It may be noted that substances such as RDX act both as fuel and as oxidiser; nitrocellulose acts as a fuel, oxidiser and a plasticiser, whereas gunpowder uses charcoal as a fuel and potassium nitrate as the oxidiser, sulphur is added as a catalyst, although it participates in the reaction. One of the most commonly used solid propellants has the following composition: ammonium perchlorate, 70%; aluminium, 16%; elastomer polymer binder (polybutadiene, polyurethane), 14%.

Solid propellants are easier to store, handle and transport.

Spacecrafts also use liquid propellants such as nitrogen tetroxide, hydrazine, hydrogen peroxide, etc. Liquid propellants are introduced into the combustion chamber of the spacecrafts as liquids. Their storage and transportation are rather difficult.

Hybrid propellants with solid fuel and liquid or gaseous oxidisers are also used in spacecraft.

1.20 Gaseous Fuels

Gaseous fuels can be obtained in many ways:

- (a) **From nature** Examples include natural gas and methane from coal mines.
- (b) **From solid fuels** Examples include producer gas, water gas, coal gas and blast furnace gas.
- (c) **From petroleum** Examples include refinery gases, LPG and gases from oil gasification.
- (d) **By fermentation of organic wastes** Examples include biogas.

1.21 Natural Gas

Natural gas is generally found to be associated with petroleum in nature and occurs near coal mines or oil fields. It is used not only as a fuel for domestic and industrial purposes but also as a raw material in various chemical syntheses. Natural gas that is derived from oil wells may be dry or wet. When natural gas is found to be associated with petroleum in oil well (it may be found dissolved in oil or may be present as a gas cap above the oil) it is called associated natural gas which is also termed as 'wet gas'. It is obtained from the oil-producing wells and is a mixture of methane and higher hydrocarbons such as n-propane, n-butane, isobutane, isopentane, etc. Wet natural gas contains less than 85% methane. Natural gas may also be present in reservoirs where there is no oil. This gas is called non associated natural gas or 'dry gas'. Dry gas is almost pure methane and once compressed it can be used directly as vehicle fuel. About 60% of the world's natural gas is non associated or dry natural gas. It may be noted here that the terms wet and dry have nothing to do with water, they only refer to the presence or absence of condensable hydrocarbons.

The approximate composition of natural gas is $\text{CH}_4 = 70\text{--}90\%$; $\text{C}_2\text{H}_6 = 5\text{--}10\%$; $\text{H}_2 = 3\%$; remaining CO and CO_2 . Apart from ethane natural gas also contains propane, butane, pentane, hexane, nitrogen and sometimes noble gases like helium are also present.

Its calorific value varies from 12000 to 14000 kcal/m³.

Natural gas has wide ranging applications. It finds its use as a fuel in domestic and industrial sectors as well as in motor vehicles. It is also used to prepare ethane, propane, butane, acetic acid, etc. It serves as an important ingredient in the manufacture of various fertilizers, plastics, pharmaceuticals, fabrics and antifreeze agents.

1.22 Compressed Natural Gas (CNG)

It is obtained by compressing natural gas to a high pressure of about 1000 atmospheres. These days CNG is used as substitute for petrol and diesel. It is very economical and a clean fuel. It is better than LPG and is preferred over gasoline or LPG because

- It is safer than gasoline or diesel because its ignition temperature is higher than gasoline or diesel.
- It is lighter than air and disperses easily in air, minimising the risk of ignition. LPG being heavier than air settles at the ground level and hence is risky.
- As compared to gasoline, CNG produces lesser carbon monoxide on combustion.
- CNG-operated vehicles do not emit forbidden pollutants such as smoke, SO_2 , SO_3 , C_6H_6 , HCHO , etc.

1.23 Liquefied Petroleum Gas

Liquefied petroleum gas (LPG) is commonly used as a domestic fuel, industrial fuel and a fuel in motor vehicles. Chemically, it is a mixture of C_3 and C_4 hydrocarbons of the corresponding alkane and alkene series. It is generally obtained as a by-product during the cracking of heavy oils or from natural gas. The gas obtained by cracking is dehydrated, desulphurised and bottled in cylinders under high pressure. Highly odorous ethylmercaptan is added to it to detect leakage.

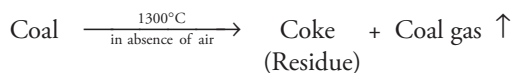
Composition LPG mainly contains paraffin hydrocarbons up to C_4 and its main constituents are n-butane, isobutane, butylene and propane with little or no propylene or ethane. These hydrocarbons exist in gaseous form under atmospheric pressure but can be liquified readily under pressure.

Properties

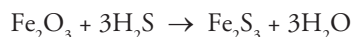
- It is a colourless, tasteless gas having very faint odour.
- It is 1.5–2.0 times heavier than air and can be easily liquefied at moderate pressure. The liquid is immediately transformed into vapour as soon as the pressure is released.
- It is non-toxic and non poisonous but being heavier than air it pushes the air out of the room and can lead to suffocation.
- It is inflammable and has a high calorific value of nearly 27800 kcal/m³. This is nearly three times the calorific value of natural gas and seven times that of coal gas.

1.24 Coal Gas

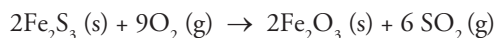
It is obtained when coal is heated in the absence of air at about 1300 °C in gas retort or coke ovens. The fuel used for the purpose is a mixture of producer gas and air.



Tar, NH_3 , naphthalene and benzene are removed by passing the outcoming gases through water, cold water, petroleum and creosote oil, respectively. H_2S is removed by passing it over moist ferric oxide contained in a purifier (Fig. 1.17).

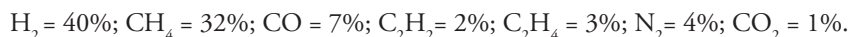


When iron oxide is exhausted it is taken out from the purifier and exposed to air where it gets oxidised to ferric oxide.



The purified coal gas is finally stored over water in gas holders.

Coal gas is a colorless gas having a characteristic odour. It is lighter than air and burns with a long smoky flame. Its average composition is



Its calorific value is 4900 kcal/m³.

Uses

- As illuminant in cities and towns.
- As a fuel.
- As a raw material for ammonia production.
- In metallurgical operations for providing a reducing atmosphere.

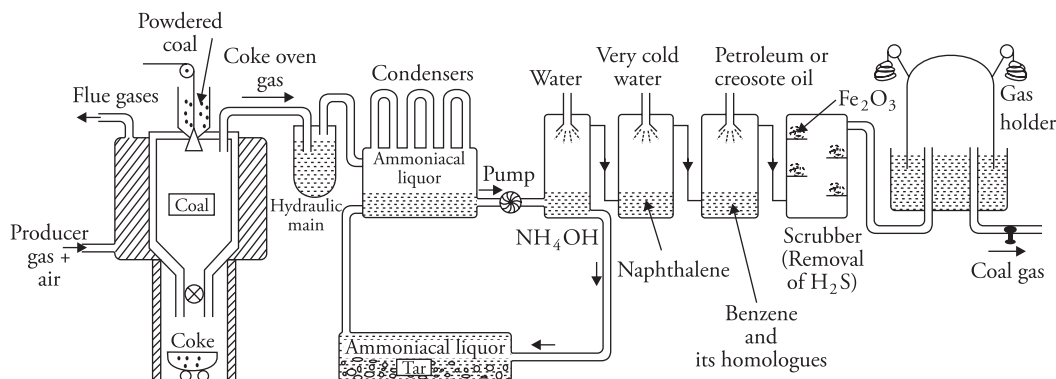


Figure 1.17 Manufacture of coal gas

1.25 Oil Gas

It is obtained by the cracking of kerosene oil.

Production

The plant used for the purpose consists of a strong cast iron retort enclosed in a coal-fired furnace. A bonnet is fitted at the mouth of the retort through a water seal. A pipe from the hydraulic main leads to the gas holder. This pipe has a testing tap from where the samples of gas can be taken for testing (Fig. 1.18).

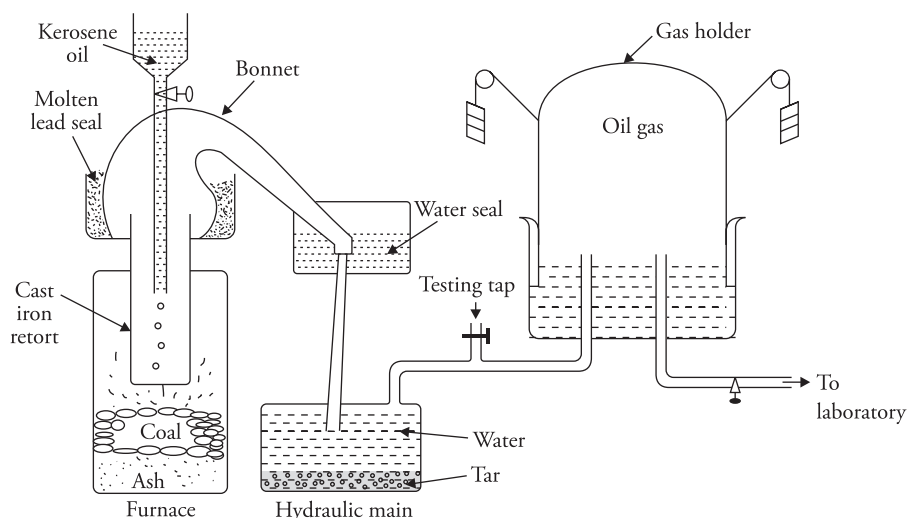
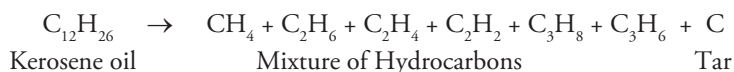


Figure 1.18 Manufacture of oil gas

Working

The retort is heated to red hot and a stream of oil is continuously allowed to fall on the red-hot bottom of the retort. The oil on coming in contact with the red-hot bottom immediately gets cracked into a number of lower gaseous hydrocarbons.



The gaseous mixture so obtained passes through the bonnet to a hydraulic tank (tank containing water) where tar gets condensed. Then at the testing tap, proper cracking of the gas is estimated from the color of the gas. A good oil gas should have a golden color. By properly adjusting the supply of air, golden color is obtained. The gas is finally stored over water in gas holders.

The yield of gas is 40–50% and its calorific value is about 4500–5400 kcal/m³.

Approximate composition of oil gas

Constituent	Methane (CH ₄)	Hydrogen (H ₂)	Carbon monoxide (CO)	Carbon dioxide (CO ₂)
Percentage	25–30%	50–55%	10–15%	3%

Applications

- It is used as laboratory gas.
- It is also used to improve the calorific value of water gas and the mixture of the two gases is called carbureted water gas.

1.26 Producer Gas

It is a mixture of carbon monoxide (combustible gas) and nitrogen (non-combustible gas).

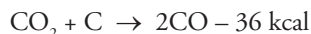
Preparation It is prepared by passing air mixed with a little steam (about 0.35 kg/kg of coal) over red hot coal or coke bed maintained at 1100 °C in a special reactor called 'gas producer'. Gas producer is a steel vessel, about 3 m in diameter and 4 m in height. It is lined inside with refractory bricks to maintain a temperature of about 1100 °C. At the top of the reactor there is a cup and cone arrangement for feeding the charge and a side opening for the exit of producer gas. At the base there is inlet for air and steam and an exit for the ash formed (Fig. 1.19).

Reaction When a mixture of air and steam is passed over red hot coke or coal bed at 1100 °C in gas producer the following reactions take place in different zones of the fuel bed

- Ash zone** It is the lowest zone consisting mainly ash. It is about 0.8 m thick. The function of this zone is
 - To preheat the air and steam mixture as it passes through this zone.
 - As ash is a bad conductor of heat it protects the grate (metal framework at the base for holding fuel) from intense heat of combustion.
- Combustion zone or oxidation zone** It is the zone next to the ash zone. In this zone carbon of the coal or coke burns in the presence of air to form CO and CO₂. The temperature of this zone is about 1100 °C.



- Reduction zone** Here carbon dioxide (produced in combustion zone) and steam combines with red hot coke to liberate free hydrogen and carbon monoxide:



As all the above reactions are endothermic the temperature of this zone falls to 1000 °C. For the production of producer gas only air can be used; however, the usage of steam along with air is beneficial because

- (a) It raises the content of combustible component ($\text{CO} + \text{H}_2$), thereby increasing the calorific value.
 - (b) The endothermic reaction of steam and carbon prevents the temperature from rising too high and prevents the fusion of ash and refractory lining.
4. **Distillation zone** This is the uppermost part of the fuel bed. Here ($400\text{--}800^\circ\text{C}$), the outgoing gases give a portion of their heat to the down coming coal. This along with heat radiated from the reduction zone helps to distil the fuel, thereby volatile matter of coal is removed and comes out with outgoing gas.

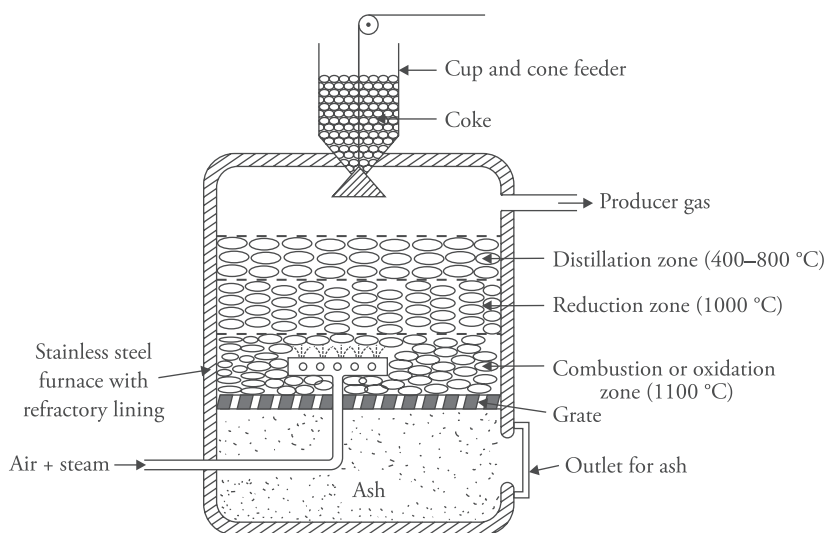


Figure 1.19 Manufacture of producer gas

Composition The average composition of producer gas is

	Combustible gases		Non-Combustible gases	
Constituent	CO	H_2	N_2	CO_2
Percentage	22–30%	8–12%	52–55%	3%

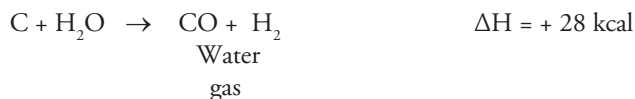
It is insoluble in water and is poisonous in nature. Its calorific value is about $900\text{--}1300\text{ kcal/m}^3$

Applications

- As a reducing agent in metallurgical operations.
- As a fuel for heating open-hearth furnaces, muffle furnace and retorts (used in coke and coal gas manufacture).

1.27 Water Gas

It burns with a blue flame and is often termed as 'blue gas'. It is a mixture of carbon monoxide and hydrogen with little amount of non-combustible gases such as carbon dioxide and nitrogen. Its calorific value is nearly 2800 kcal/m³ and is prepared by passing steam over red hot coke at about 1000 °C.



The above reaction being endothermic requires lot of heat to maintain the temperature of the furnace. If this heat is supplied from an external source the process would become uneconomical; hence, the reaction is carried out in two steps. In the first step air is blown to generate heat, and in the second step steam is blown and the formation of water gas takes place with the absorption of heat. These two steps are called *blow and run periods*, respectively.

Manufacture The gas generator is made up of steel with a refractory lining. It has a cup and cone arrangement at the top for feeding the coke. At the bottom it is provided with two separate inlets for steam and air supply. There is an outlet for the removal of ash at the bottom and for the exit of water gas near the top (Fig. 1.20).

The following reactions are involved

1. Air is passed through the coke bed when the carbon of the coke burns in the presence of the oxygen in air to produce carbon dioxide. This reaction is exothermic and the temperature of the fuel bed rises to 1000 °C. This is the *blow step* of the cyclic process.
2. When a sufficiently high temperature is attained the supply of air is cut off and then steam is blown through the red hot bed of coke. Steam combines with coke to form water gas.



The second step is the *run step* of the cyclic process. This step is endothermic and hence the temperature again begins to drop. Again the supply of steam is stopped and air is supplied. The cycle is repeated alternately to maintain the required temperature.

Composition

The approximate composition of water gas is



Uses

Water gas is used as a fuel in furnace; it is used in Fischer–Tropsch process for the manufacture of synthetic petrol. Its mixture with hydrogen is used for the manufacture of methanol.

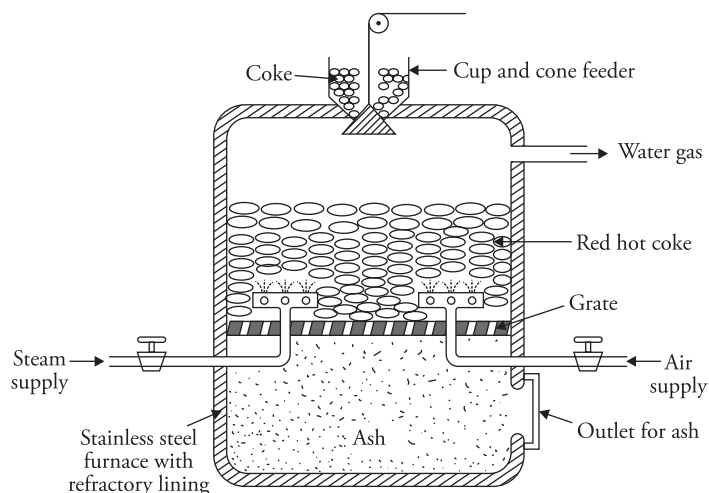


Figure 1.20 Manufacture of water gas

Carbureted water gas The calorific value of water gas is very low (2800 kcal/m^3). Its calorific value can be increased by mixing it with gaseous hydrocarbons obtained by the cracking of crude oils. This enhances the calorific value of water gas to 4500 kcal/m^3 . The average composition of carbureted water gas is

$\text{CO} = 23 - 28\%$, $\text{H}_2 = 34 - 38\%$; Saturated and unsaturated hydrocarbons = $30 - 48\%$;
 $\text{CO}_2 = 0.2 - 2.5\%$; $\text{N}_2 = 2.5 - 5\%$

1.28 Analysis of Flue Gas

The gaseous products formed after combustion of a fuel are called *flue gases*. The flue gases consist of carbon dioxide, sulphur dioxide, carbon monoxide, nitrogen, water vapor and excess oxygen.

For proper and efficient combustion of a fuel, it is essential that the fuel comes in contact with sufficient quantity of air to burn all the combustible matter present. The analysis of flue gases gives an idea about the complete or incomplete combustion process. The analysis is usually carried out to measure the amount of CO_2 , CO , O_2 and N_2 in the flue gases. Thus,

1. If the analysis shows the presence of CO , it indicates the incomplete combustion of the fuel or shortage of oxygen. Hence, the supply of oxygen should be increased or the supply of fuel should be reduced.
2. If the flue gases contain a considerable amount of oxygen, it indicates that the combustion is complete but the supply of air is very much in excess. Ordinarily, 50–100% excess air is generally supplied but too much excess air results in loss of heat. In such cases, the supply of air is reduced or the rate of supply of fuel is increased.

3. If the analysis shows the presence of oxygen and carbon monoxide, it indicates that the combustion is irregular and non-uniform, that is in some parts of the furnace, there is excess air and in some other parts the supply of air is insufficient. Hence, the supply of air is to be regulated in all the parts of the furnace. The analysis of flue gases is carried out with the help of Orsat's apparatus.

Orsat Apparatus

Construction It consists of a horizontal tube having a three-way stop cock at one end and a graduated burette at other end. The free end of the stop cock is further connected to a U-tube containing fused CaCl_2 and glass wool (to remove moisture and smoke particles from the flue gas). The burette is surrounded by a water jacket to keep the temperature of the gas constant during the experiment. The lower end of the burette is connected to a water reservoir by means of a long rubber tubing. The level of water in the reservoir can be raised or lowered by raising or lowering the water reservoir (Fig. 1.21).

The horizontal tube is connected in series to a set of three absorption bulbs A, B and C each through a stop cock. The absorption bulbs are filled with glass tubes so that the surface area of contact between the gas and the solution is increased.

The absorption bulbs have solutions for the absorption of CO_2 , O_2 and CO , respectively.

- Bulb A contains KOH to absorb CO_2 (250 g KOH in 500 mL of boiled distilled water).
- Bulb B contains a solution of alkaline pyrogalllic acid (25 g of pyrogalllic acid + 200 g KOH in 500 mL of distilled water). It can absorb CO_2 and O_2 .
- Bulb C contains 'ammoniacal cuprous chloride solution' (100 g cuprous chloride + 125 mL liquor ammonia + 375 mL of water). It can absorb CO , CO_2 and O_2 .

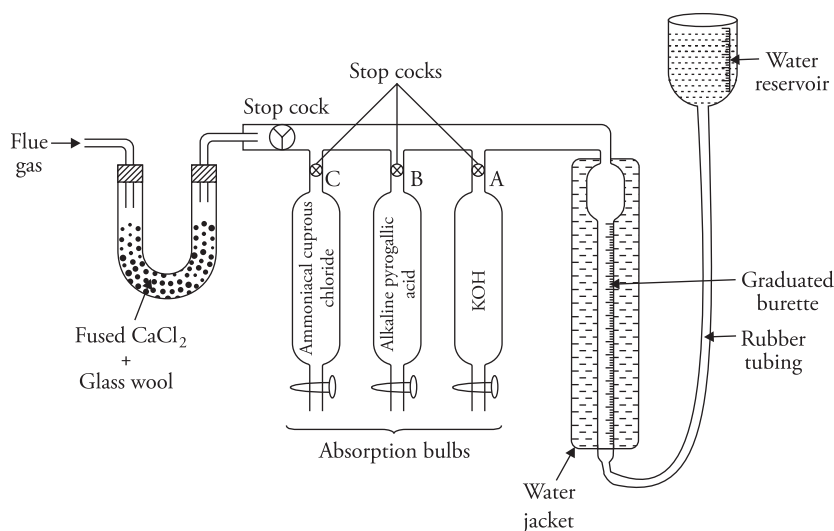


Figure 1.21 Orsat's apparatus

Working

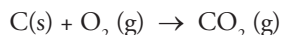
- (i) The whole apparatus is cleaned thoroughly. The stoppers are greased and are tested for their air tightness. The bulbs A, B and C are filled with their respective solutions and their stop cocks are closed. The jacket and leveling reservoir are filled with water.
- (ii) The three-way stop cock is opened to atmosphere and the reservoir is raised till the burette is completely filled with water and air present in it is removed.
- (iii) The three-way stop cock is now connected to the flue gas supply and the reservoir is lowered. The flue gas to be analysed enters in after passing through the CaCl_2 U-tube, which absorbs moisture present in the flue gas. However, this flue gas is mixed with air present in the apparatus and hence is expelled out by opening the three-way stop cock and raising the reservoir. This process is repeated 3–4 times to ensure complete removal of the air present in the apparatus.
- (iv) Finally, the flue gas is sucked in the burette and the volume is adjusted to 100 mL at atmospheric pressure. This is done by adjusting the height of the leveling reservoir. The three-way stop cock is opened to the atmosphere and the reservoir is carefully raised, till the level of water in it is the same as in the burette which stands at 100 mL mark. The three way stop cock is then closed.
- (v) Now the stopper of bulb A (containing KOH) is opened and the water reservoir is raised. The flue gas is again sent to the burette by lowering the reservoir. By raising the reservoir several times complete absorption of CO_2 is ensured. The unabsorbed gases are finally taken back to the burette, till the level of solution in the CO_2 absorption bulb stands at a constant mark. After this the stop cock is closed. The levels of water in the burette and reservoir are equalised and the volume of the residual gases is noted. The decrease in volume gives the volume of CO_2 in 100 mL of the flue gas sample.
- (vi) Now the stop cock B is opened and the process is repeated as mentioned above. The decrease in volume gives the volume of O_2 in 100 mL of flue gas.
- (vii) Similarly the flue gas is passed through the bulb C to determine the amount of CO.
- (viii) The gas remaining in the burette after the absorption of CO_2 , O_2 and CO is taken as nitrogen.

Precautions

1. The flue gases should be passed first in bulb A (KOH solution), then bulb B (pyrogalllic acid solution) and then through bulb C (ammoniacal cuprous chloride solution) because KOH absorbs CO_2 , pyrogalllic acid absorbs $\text{CO}_2 + \text{O}_2$ and ammoniacal Cu_2Cl_2 absorbs $\text{CO}_2 + \text{O}_2 + \text{CO}$.
2. CO should be determined carefully as its amount is very small.
3. All the air should be expelled from the apparatus before starting the experiment.

1.29 Combustion Calculations

Combustion is a chemical reaction accompanied by the liberation of heat. It is an exothermic process. For example



$$\Delta H = -97 \text{ kcal.}$$

To ensure complete combustion of a fuel, it is essential that appropriate amount of oxygen and air is supplied. If the amount of oxygen and air supplied is insufficient, complete combustion will not take place and too much excess should also not be supplied.

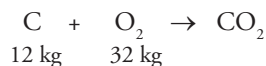
Hence in any industrial and metallurgical processes it is essential to calculate the minimum amount of oxygen and air required for the complete combustion of the fuel used.

Calculation of air required for the combustion of solid and liquid fuels

The elements generally present in the fuel are carbon, hydrogen, oxygen, nitrogen and sulphur. During combustion of the fuel these elements combine with oxygen. If the percentage composition of fuel is known, the amount of oxygen required for combustion can be calculated. The method of calculation of air is summarised below

- (i) Weight of each constituent present per kilogram of the fuel is calculated from the percentage composition of the fuel. Let the weight of carbon, hydrogen, oxygen, and sulphur in one kg of the fuel be C kg, H kg, O kg and S kg, respectively.
- (ii) The quantity of oxygen required for the combustion of C kg of carbon, H kg of hydrogen, S kg of sulphur can be calculated with the help of the equations given below

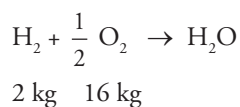
Combustion of carbon



12 kg of carbon requires 32 kg of oxygen.

C kg of carbon requires $\frac{32}{12} \times C$ kg or $2.67 C$ kg of oxygen.

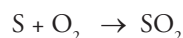
Combustion of hydrogen



2 kg of hydrogen requires 16 kg of oxygen.

H kg of hydrogen requires $\frac{16}{2} \times H$ kg or $8 H$ kg of oxygen

Combustion of sulphur



32 kg of sulphur requires 32 kg of oxygen.

S kg of sulphur requires $\frac{32}{32} \times S$ kg or $1 S$ kg of oxygen.

The other constituents present in fuel do not require oxygen.

Thus, total quantity of oxygen required for the combustion of 1 kg of fuel will be

$$(2.67 C + 8 H + S) \text{ kg.}$$

If oxygen is already present in the fuel, the quantity of oxygen to be supplied from air

(Total oxygen required – O_2 present in fuel)

$$(2.67 C + 8 H + S - O) \text{ kg}$$

So, minimum quantity of O_2 or the theoretical amount of O_2 required for the complete combustion of 1 kg of a fuel

$$= (2.67 C + 8 H + S - O) \text{ kg}$$

As air contains 23% oxygen by weight; hence, minimum weight of air required for combustion

$$= (2.67 C + 8 H + S - O) \frac{100}{23} \text{ kg.}$$

Calculation of volume of oxygen or air required

At certain temperature and pressure, the mass of any gas can be converted into its volume and vice versa by using the gas equation. The volume of oxygen or air required for the combustion of fuel is calculated

$$PV = \frac{W}{M} \times RT$$

where,

P = pressure of gas in atmosphere; V = volume of gas

R = gas constant; T = temperature in K

W = mass of gas; M = molecular mass of the gas.

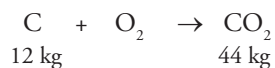
Alternatively the weight of oxygen required can be converted into its volume at normal temperature and pressure. 22.4 liters of any gas at NTP has a mass equal to its gram molecular weight and air contains 21% oxygen by volume. Hence, the volume of air required can also be calculated.

Calculation of quantity of flue gases

The gases coming out after combustion CO_2 , SO_2 , CO, O_2 , N_2 are called flue gases. The water vapours formed condense as the gases cool down while the ash is excluded as it does not take part in combustion. Therefore, water vapours and ash are not included while calculating the percentage of dry combustion products.

Calculation of the flue gases when minimum amount of air is supplied

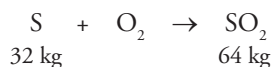
All the O_2 of air will be used in combustion of carbon and sulphur while N_2 in air remains unreacted. Let 1 kg of fuel contain C kg of carbon and S kg of sulphur. The weight of CO_2 and SO_2 thus formed by the combustion of fuel is calculated as follows



12 kg of carbon on combustion gives 44 kg of carbon dioxide.

Therefore, C kg of carbon gives $\frac{44}{12} \times C$ kg of CO_2 .

Similarly,



32 kg of sulphur on combustion gives 64 kg of sulphur dioxide.

S kg of sulphur gives $\frac{64}{32} \times S$ kg or 2 S kg of SO_2 .

Weight of $N_2 = \frac{77}{100} \times \text{weight of air supplied} + \text{weight of } N_2 \text{ per kg of fuel.}$

Total weight of dry flue gases formed by the combustion of 1 kg of fuel =

Weight of CO_2 + weight of SO_2 + weight of N_2

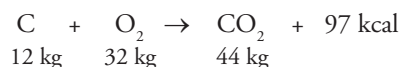
The % composition by weight of each constituent can then be calculated.

Calculation of the flue gases when excess of air is supplied

- (i) CO_2 and SO_2 are calculated as mentioned above.
 - (ii) N_2 in flue gas = N_2 of total air supplied + N_2 present in the fuel.
 - (iii) When excess air is supplied the flue gas will contain O_2 of excess air.
- Hence, the total weight of flue gas per kg of the fuel (when excess air is supplied)
- = weight of CO_2 + weight of SO_2 + weight of N_2 + weight of O_2

Important facts for combustion calculation

- (i) Substances always combine in definite proportion.



(ii) Composition of air	% oxygen	% nitrogen
By volume	21	79
By weight	23	77

Thus, 1 kg of oxygen is supplied by $1 \times \frac{100}{23} = 4.35$ kg of air.

1 m³ of oxygen is supplied by $1 \times \frac{100}{21} = 4.76$ m³ of air.

(iii) The average molecular weight of air is taken as 28.94 g mol⁻¹

1 g mol of any gas at STP (0 °C and 760 mm pressure) occupies 22.4 L, that is weight of 22400 mL of a gas at STP is its molecular mass.

(iv) The mass of any gas can be converted into its volume by the gas law

PV = nRT where *n* is the number of moles of the gas.

(v) Minimum oxygen required for combustion = Theoretical oxygen required – O₂ present in fuel.

(vi) Combustion seldom takes place efficiently with minimum weight of oxygen or air. An excess of air has to be supplied for proper combustion.

$$\% \text{ Excess air} = \frac{\text{Actual air used} - \text{Minimum weight of air required}}{\text{Minimum weight of air required}} \times 100$$

(vii) Actual amount of air supplied is found out by taking excess air into consideration.

(ix) To convert weight into volume and vice versa the Avogadro's law is used.

(x) Let the weight of air required = *x* kg

According to Avogadro's law,

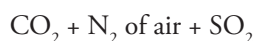
28.94 g air occupies 22.4 L

or, 28.94 kg of air occupies 22.4 m³.

$$x \text{ kg of air occupies } \frac{22.4}{28.94} \times x \text{ m}^3 \text{ volume}$$

(Since, 1 m³ = 1000 L and 1 kg = 1000 g)

If minimum weight of air is used for combustion the dry flue gas will contain



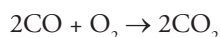
(xi) If excess air is used for combustion then the dry flue gases will contain

$\text{CO}_2 + \text{SO}_2 + \text{N}_2$ of the total air supplied + O_2 from excess air.

Combustion of gaseous fuel

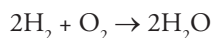
CO , H_2 and hydrocarbons such as CH_4 , C_2H_6 , etc. are the main constituents of common gaseous fuels. The quantity of O_2 or air required in such cases is measured by the volume according to the combustion reactions of the constituents.

Combustion of carbon monoxide



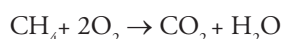
Thus, 2 volume of CO combine with 1 volume of O_2 to give 2 volume of CO_2

Combustion of H_2



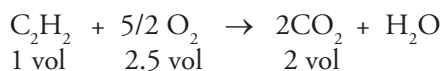
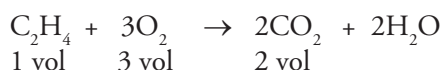
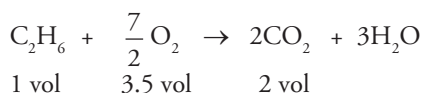
Here 2 volumes of H_2 combines with 1 volume of O_2

Combustion of CH_4



1 volume of methane reacts with 2 volumes of O_2

Similarly, other combustion reactions are



The other constituents such as CO_2 and N_2 do not require any oxygen.

If the percentage composition of a gaseous fuel is known then the amount of O_2 required for combustion can be calculated with the help of the combustion equations. If the fuel already contains oxygen then that amount is subtracted from the total O_2 required. As air contains 21% O_2 by volume, the volume of air required can be calculated by multiplying with 100/21.

To determine the percentage composition of dry flue gases the volume of CO_2 is also calculated as above. N_2 of the fuel comes out along with the flue gases; hence, the total N_2 in flue gases is N_2 in fuel + N_2 in air supplied for combustion. If excess air is supplied then the volume of O_2 present in the excess air is also taken into account. Percentage composition of dry flue gases is then calculated. Dry flue gases do not contain water vapour as they condense on cooling, hence, H_2O is not included in the calculation of the % composition of dry flue gases.

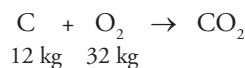
Problems Based on Weight Calculations

Solved Examples

1. Calculate the weight and volume of air required for the combustion of 3 kg of carbon.

Solution

Combustion reaction



Weight of oxygen required to burn 12 kg C = 32 kg

Weight of oxygen required to burn 3 kg C = $\frac{32}{12} \times 3 = 8 \text{ kg}$

As, air contains 23% oxygen by weight

Therefore, weight of air required = $8 \times \frac{100}{23} = 34.783 \text{ kg} = 34783 \text{ g}$

Volume of air required

as, 1 mole of any gas at STP occupies 22.4 L

Therefore, volume occupied by 1 mole air = 28.94 g air = 22.4 L

(molecular weight of air = 28.94 g)

Volume occupied by 34783 g of air = $\frac{22.4}{28.94} \times 34783$
 $= 26.92 \times 10^3 \text{ L} = 26.92 \text{ m}^3$
 (Since 1 L = 10^{-3} m^3)

2. Calculate the mass of air needed for the complete combustion of 5 kg of coal containing C = 80%; H = 15%, O = rest

Solution

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O ₂ required
C	0.80 kg	$C + O_2 \rightarrow CO_2$	$0.80 \times \frac{32}{12} = 2.133 \text{ kg}$
H	0.15 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.15 \times \frac{16}{2} = 1.20 \text{ kg}$
O	$1.00 - (0.80 + 0.15) = 0.05 \text{ kg}$		
			Total O ₂ required = $2.133 + 1.20 = 3.333 \text{ kg}$

Oxygen required from air = Total O₂ required – O₂ in fuel

$$= 3.333 - 0.05 = 3.283 \text{ kg}$$

$$\text{Weight of air required for combustion of 1 kg of fuel} = 3.283 \times \frac{100}{23} = 14.27 \text{ kg}$$

$$\text{Therefore, weight of air required for combustion of 5 kg of fuel} = 14.27 \times 5 = 71.369 \text{ kg}$$

[Ans = 71.369 kg]

3. A sample of coal was found to have the following composition by weight

C = 75%; H = 5.2%; O = 12.1%; N = 3.2% and ash = 4.5%

Calculate (i) minimum amount of O₂ and air necessary for complete combustion of 1 kg of coal; (ii) weight of air required if 40% excess air is supplied.

Solution

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O ₂ required
C	0.75 kg	$C + O_2 \rightarrow CO_2$	$0.75 \times \frac{32}{12} = 2 \text{ kg}$
H	0.052 kg	$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$	$0.052 \times \frac{16}{2} = 0.416 \text{ kg}$

O	0.121 kg	–	–
N	0.032 kg	–	–
Ash	0.045 kg	–	–
		–	Total O ₂ required = 2.416 kg

O₂ required from air = Total O₂ required – O₂ in fuel

$$= 2.416 \text{ kg} - 0.121 \text{ kg} = 2.295 \text{ kg}$$

$$\text{Minimum weight of air required} = 2.295 \times \frac{100}{23} = 9.978 \text{ kg.}$$

$$\text{Weight of excess air} = 9.978 \times \frac{40}{100} = 3.9912 \text{ kg}$$

$$\text{Total air supplied} = 9.978 + 3.9912 = 13.969 \text{ kg.}$$

[Ans = 13.969 kg]

4. A fuel is found to contain C = 90%; H = 6.0%; S = 2.5%; O = 1.0% and ash = 0.5%. Calculate the amount of air required for complete combustion of 1 kg of fuel. If 25% excess air is used for combustion, calculate the percentage composition of the dry products of combustion.

Solution

Constituent	Amount per kg of the coal sample	Combustion reaction	Weight of O ₂ required	Weight of dry flue gas
C	0.90 kg	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$0.90 \times \frac{32}{12} = 2.4 \text{ kg}$	$0.90 \times \frac{44}{12} = 3.3 \text{ kg}$
H	0.06 kg	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$0.06 \times \frac{16}{2} = 0.48 \text{ kg}$	H ₂ O does not constitute dry flue gas
S	0.025 kg	$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$	$0.025 \times \frac{32}{32} = 0.025 \text{ kg}$	$0.025 \times \frac{64}{32} = 0.05 \text{ kg}$
O	0.01 kg	–	–	–
Ash	0.005 kg	–	–	–
		–	Total O ₂ required = 2.4 + 0.48 + 0.025 kg = 2.905 kg	

$$\begin{aligned}\text{O}_2 \text{ required from air} &= \text{Total O}_2 \text{ required} - \text{O}_2 \text{ in fuel} \\ &= 2.905 - 0.01 = 2.895 \text{ kg}\end{aligned}$$

$$\text{Minimum weight of air required for combustion} \quad 2.895 \times \frac{100}{23} = 12.587 \text{ kg}$$

According to the question 25% excess air is supplied

$$\text{Excess air} = 12.587 \times \frac{25}{100} = 3.147 \text{ kg}$$

$$\begin{aligned}\text{Total air supplied} &= 12.587 \text{ kg} + 3.147 \text{ kg} \\ &= 15.734 \text{ kg}\end{aligned}$$

(i) Calculation of dry products in the flue gases

The flue gases contains CO_2 , SO_2 , O_2 from excess air and N_2 from the total air supplied.

$$\text{Weight of CO}_2 = 3.3 \text{ kg}$$

$$\text{Weight of SO}_2 = 0.05 \text{ kg}$$

$$\text{Weight of O}_2 = 3.147 \times \frac{23}{100} = 0.724 \text{ kg}$$

$$\text{Weight of N}_2 = 15.734 \times \frac{77}{100} = 12.115 \text{ kg}$$

$$\begin{aligned}\text{Total weight of flue gases} &= 3.3 + 0.05 + 0.724 + 12.115 \\ &= 16.189 \text{ kg}\end{aligned}$$

Percentage composition of dry flue gases

$$\% \text{ CO}_2 = \frac{3.3}{16.189} \times 100 = 20.38\%$$

$$\% \text{ SO}_2 = \frac{0.05}{16.189} \times 100 = 0.309\%$$

$$\% \text{ O}_2 = \frac{0.724}{16.189} \times 100 = 4.47\%$$

$$\% \text{ N}_2 = \frac{12.115}{16.189} \times 100 = 74.835\%$$

Practice problems

1. A fuel is found to contain C = 90%; H = 3.5%; S = 0.5%; H₂O = 1.0%; N = 0.5% and ash = rest. Calculate the minimum amount of air required for complete combustion of 1 kg of fuel.

[Ans = 11.6739 kg]

2. A sample of coal is found to contain : C = 81%; H = 5.0%; S = 1%; O = 8.0%; N=1% and ash = 4%. Calculate the amount of air required for complete combustion of 1 kg of fuel. Also calculate the percentage composition by weight of the dry products of combustion. Oxygen in air is 23% by weight.

[Ans (i) 10.826 kg; (ii) CO₂ = 26.22%; N₂ = 73.005%; SO₂ = 0.1765%]

3. A sample of coal was found to contain: C = 80%; H = 5.0%; N= 2%; O = 1.0% and remaining ash.

- Calculate the amount of air required for complete combustion of 1 kg of coal sample.
- If 45% excess air is supplied, estimate the percentage composition of the dry products of combustion.

[Ans Air = 10.9708 kg; % CO₂ = 17.976%; N₂ = 75.067%; O₂ = 6.956%]

Problems based on volume calculations**Solved Problems**

1. A gas used in internal combustion engine had the following composition by volume : H₂ = 45%; CH₄ = 36%; CO = 15%; N₂ = 4%. Find the volume of air required for the combustion of 1 m³ of the gas.

Solution

Constituent	Amount in 1m ³ of the fuel	Combustion reaction	Volume of O ₂ required(m ³)
H ₂	0.45 m ³	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	45 × 0.5 = 0.225
CH ₄	0.36 m ³	$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	0.36 × 2 = 0.72
CO	0.15 m ³	$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	0.15 × 0.5 = 0.075
N ₂	0.04 m ³		
			Total = 1.020

$$\begin{aligned} \text{Therefore volume of air required per m}^3 \text{ of the gas} &= 1.020 \text{ m}^3 \times \frac{100}{21} \\ &= 4.857 \text{ m}^3 \end{aligned}$$

2. A given sample of petrol contains H = 15.4% and C = 84.6%. Calculate the minimum volume of O₂ required for the combustion of this sample.

Solution

Constituent	Amount in 1 kg of petrol	Combustion reaction	Weight of O ₂ required(kg)
H	0.154 kg	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	$0.154 \times \frac{16}{2} = 1.232 \text{ kg}$
C	0.846 kg	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$0.846 \times \frac{32}{12} = 2.256 \text{ kg}$
			Total O ₂ reqd = 3.488 kg

Weight of O₂ required for combustion of 1 kg fuel = 3.488 kg
= 3488 g.

Since 1 mole = 32 g of O₂ at NTP occupies 22.4 L

Therefore 3488 g of O₂ at NTP occupies = $\frac{22.4}{32} \times 3488$
= 2441.6 L
= 2.441 m³

(Since 1000 L = 1 m³)

3. A gaseous fuel has the following composition by volume – CH₄ = 20%; CO = 10%;

CO₂ = 5%; O₂ = 2%; C₂H₄ = 5%; C₃H₈ = 8%, rest N₂. Calculate the volume of air supplied per m³ of fuel and the % composition of dry flue gases.

Solution

Constituents	Volume in 1 m ³ of gas	Combustion Reaction	O ₂ required (in m ³)	Volume of dry flue gases(m ³)
CH ₄	0.20 m ³	$\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	$0.20 \times 2 = 0.40 \text{ m}^3$	CO ₂ = 0.20 × 1 = 0.20 m ³
CO	0.10 m ³	$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	$0.10 \times \frac{1}{2} = 0.05 \text{ m}^3$	CO ₂ = 0.10 × 1 = 0.10 m ³
CO ₂	0.05 m ³	–	–	CO ₂ = 0.05 m ³
O ₂	0.02 m ³	–	–	
C ₂ H ₄	0.05 m ³	$\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$	$0.05 \times 3 = 0.15 \text{ m}^3$	CO ₂ = 0.05 × 2 = 0.10 m ³
C ₃ H ₈	0.08 m ³	$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$	$0.08 \times 5 = 0.40 \text{ m}^3$	CO ₂ = 0.08 × 3 = 0.24 m ³
N ₂	0.50	–	–	$\text{N}_2 = 0.50 + \frac{79}{100} \times 4.67 = 4.19 \text{ m}^3$
			Total O ₂ reqd = 1.0 m ³ O ₂ in fuel = 0.020 m ³ Net O ₂ reqd. = 0.98 m ³	

$$\text{Volume of air required for the combustion of } 1 \text{ m}^3 \text{ of fuel} = 0.98 \times \frac{100}{21} = 4.67 \text{ m}^3$$

Calculation of dry flue gases

$$\text{CO}_2 = (0.20 + 0.10 + 0.05 + 0.10 + 0.24) \text{ m}^3 = 0.69 \text{ m}^3$$

$$\text{N}_2 = \text{N}_2 (\text{fuel}) + \text{N}_2 (\text{from air}) = 4.19 \text{ m}^3$$

$$\text{Total volume of dry products} = 0.69 + 4.19 = 4.88 \text{ m}^3$$

$$\% \text{ CO}_2 = \frac{0.69}{4.88} \times 100 = 14.139\%$$

$$\% \text{ N}_2 = \frac{4.19}{4.88} \times 100 = 85.861\%$$

4. A gaseous fuel has the following composition by volume – $\text{CH}_4 = 4.0\%$; $\text{CO} = 26\%$; $\text{CO}_2 = 10\%$; $\text{H}_2 = 10\%$; $\text{N}_2 = 50\%$. If 20% excess air is supplied calculate the volume of air supplied and the % composition of dry flue gases.

Solution

Constituents	Volume in 1 m ³ of gas	Combustion Reaction	O ₂ required (in m ³)	Volume of dry flue gases(m ³)
CH ₄	0.04 m ³	CH ₄ + 2O ₂ → CO ₂ + 2H ₂ O	0.04 × 2 = 0.08 m ³	CO ₂ = 0.04 × 1 = 0.04 m ³
CO	0.26 m ³	CO + $\frac{1}{2}$ O ₂ → CO ₂	$0.26 \times \frac{1}{2} = 0.13 \text{ m}^3$	CO ₂ = 0.26 × 1 = 0.26 m ³
H ₂	0.10 m ³	H ₂ + $\frac{1}{2}$ O ₂ → H ₂ O	$0.10 \times \frac{1}{2} = 0.05 \text{ m}^3$	
CO ₂	0.10 m ³	–	–	CO ₂ = 0.10 m ³
N ₂	0.50 m ³	–	–	0.50 m ³ + N ₂ in total air supplied
			Volume of O ₂ required = 0.260 m ³	Total CO ₂ in flue gas = 0.40 m ³

$$\text{Minimum volume of air required} = 0.260 \times \frac{100}{21} = 1.238 \text{ m}^3$$

$$\text{Excess air} = 1.238 \times \frac{20}{100} = 0.2476 \text{ m}^3$$

$$\text{Total air supplied} = 1.238 \text{ m}^3 + 0.2476 \text{ m}^3 = 1.4856 \text{ m}^3$$

Calculation of volume of dry flue gases

The flue gas contains CO₂, O₂ from excess air and N₂ of fuel + N₂ of total air supplied.

$$\text{CO}_2 = 0.40 \text{ m}^3$$

$$\text{O}_2 = 0.2476 \times \frac{21}{100} = 0.052 \text{ m}^3$$

$$\text{N}_2 = 0.50 \text{ m}^3 \text{ (of fuel gas)} + 1.4856 \times \frac{79}{100} \text{ (from total air supplied)}$$

$$\text{N}_2 = 0.50 + 1.1174 = 1.674 \text{ m}^3.$$

$$\text{Total volume of dry flue gases} = (0.40 + 0.052 + 1.674) \text{ m}^3 = 2.126 \text{ m}^3$$

$$\% \text{CO}_2 = \frac{0.40}{2.126} \times 100 = 18.81\%$$

$$\% \text{O}_2 = \frac{0.052}{2.126} \times 100 = 2.446\%$$

$$\% \text{N}_2 = \frac{1.674}{2.126} \times 100 = 78.74\%$$

Practice problems

1. Calculate the volume of air (volume % of oxygen in air = 21) required for the complete combustion of one 1 L of CO.
[Ans 2.381 L]
2. Calculate the volume of air required for the complete combustion of 1 m³ of gaseous fuel having the composition CO = 46%; CH₄ = 10%; H₂ = 40%; C₂H₂ = 2.0%; N₂ = 1.0% and remaining being CO₂.
[Ans 3.238 m³]
3. A gaseous fuel has the following composition by volume – CH₄ = 6%; CO = 22%; O₂ = 4%; CO₂ = 4%; H₂ = 20%; N₂ = 44%. 20% excess air is used. Find the weight of air actually supplied per m³ of this gas. Molecular weight of air = 28.97.
[Ans 2143.107 g]
4. A gaseous fuel has the following composition by volume: H₂ = 25%; CH₄ = 30%; C₂H₆ = 11%; C₂H₄ = 4.5%; C₄H₈ = 2.5%; CO = 6.0%; CO₂ = 8%; O₂ = 2% and N₂ = 12%. Calculate the air fuel ratio and volumetric analysis of dry products of combustion if 40% excess air is used.
[Ans (i) 9.366:1 (ii) CO₂ = 8.415%; N₂ = 77.166%; O₂ = 14.418%]

1.30 Renewable Sources of Energy

The various energy sources such as coal, petrol, diesel discussed in the previous sections are derived by the fossilisation of plant and animal remains that got buried under the earth millions of year ago. These resources are limited, and with the rapidly growing energy demand they are likely to be depleted soon. To meet the rising global energy demand it is essential to focus on energy resources that are inexhaustible and abundantly available. These energy sources are termed as renewable or non-conventional energy sources. The various non-conventional energy sources are

1. Solar Energy
2. Wind Energy
3. Energy from water/Hydroenergy
4. Tidal Energy
5. Wave Energy
6. Energy from Biomass
7. Ocean Thermal Energy Conversion
8. Geothermal Energy
9. Hydrogen Energy

Solar Energy

Sun is the major source of energy on earth. It gives 1000 times more energy than we require. If this energy is trapped economically the energy crisis of the world would be solved. Solar energy can be used either

- (i) Directly as thermal energy like in solar cookers, solar water heater, solar dryers, desalination of sea water, etc.
- (ii) Indirectly using photovoltaic cells to convert solar energy to electricity. This is carried out by using silicon solar cells. The electricity so generated can be used for street lighting, lightning homes and buildings, running motors, pumps, electric appliances, etc.

Although the initial installation cost of a solar plant is high, it is clean energy, does not discharge harmful products in air and once installed the running cost is less and hence it is cheap.

Applications of Solar Energy

1. *Solar Water Heating* These use sunlight to heat water. A solar water heating unit comprises a blackened flat plate metal collector with an associated metal tubing facing the sun. The plate collector has a transparent cover and a layer of thermal insulation beneath it.

The metal tubing of the collector is connected by a pipe to an insulated storage tank. The collector absorbs solar radiations and transfers heat to water circulating through the tubing. This hot water is supplied to storage tank via the metal tubing.

This water heating system is used in hotels, guesthouses, tourist bungalows, hospitals, canteens as well as domestic and industrial units.

2. *Solar Cooker* Here solar energy is utilised for cooking food. A simple solar cooker is a type of a flat box which is blackened from the inner side. The solar radiations enter the box through two glass covers. These are absorbed by pots blackened from outside. The collector area is increased by providing a plane reflector mirror.
3. *Solar Lightning* Electricity is produced directly from solar energy by means of photovoltaic cells. A photovoltaic cell is an energy conversion device used to convert photons of sunlight directly into electricity. These can be used to operate irrigation pumps, rail road crossing signals, to run calculators, watches, etc. These can also be used for providing electricity in

rural areas, that is for lighting street lights. A detailed description of the principle and working of photovoltaic cells is discussed in the forthcoming sections.

4. *Solar Ponds* A solar pond is a natural or artificial body of water utilised for collecting and absorbing solar radiation and storing it as heat. It is very shallow (5-10 cm deep) and has a radiation absorbing bottom made of black plastic. It has a curved glass fiber cover over it to permit the entry of solar radiation and reduce loss of energy by radiation and convection. Loss of heat to the ground is minimised by providing a bed of insulating material under the pond.

Solar ponds utilise water for collecting and storing the solar energy which is used for many applications such as space heating, for industrial process to generate electricity by driving a turbine powered by evaporating an organic fluid with low boiling point.

5. *Solar Green Houses* These are big houses made of glass to store solar energy. They utilise the principle of greenhouse effect and are used for growing plants in cold countries or in cold climatic conditions.
6. *Solar Distillation* Solar energy is used for converting saline water into potable water in arid, semi arid and coastal areas.
7. *Solar Pumping* The power generated by solar energy is utilised for pumping water for irrigation purposes.
8. *Solar Drying of Agricultural and Animal Products* Agricultural products, fruits, etc. are dried by keeping them in big cabinets made of glass.

Solar Photovoltaic Cell

A photovoltaic cell is a device that converts solar energy directly into electrical energy. When solar radiations fall on these devices they are converted directly into dc electricity.

A solar cell is made up of light sensitive p - n junction photodiode. The photodiode is made of semiconductor materials like silicon, cadmium telluride, gallium arsenide, etc., which are capable of absorbing the photons of sunlight. However silicon solar cells are the most commonly used ones. The silicon solar cells are thin wafers of about 250 μm in thickness. A p - n junction diode is formed by doping a portion of this wafer with a trivalent impurity (for p -type) and another portion with a pentavalent impurity (for n -type) (For more details on p - n junction and semiconductors refer chapter 11 – Solid State). Metal contacts are attached on the front and back side of the cell. The front contact is in the form of metal grid to permit sunlight to pass through it and the contact on the back side completely covers the surface. The n -type silicon is on the front side and the p -type silicon is on the back side. An antireflection coating of silicon nitride or titanium oxide of about 0.1 μm thickness is applied on the top surface (Fig 1.22).

When this cell is irradiated with solar radiation on the front side (n -type silicon) electrons are knocked out from the valence band to the conduction band. These electrons flow from n -type semiconductor to p -type semiconductor thereby completing the circuit and the current flows from p -type to n -type region.

In actual practice a large number of solar cells are arranged in definite patterns to form the solar panel that helps to achieve the desired voltage.

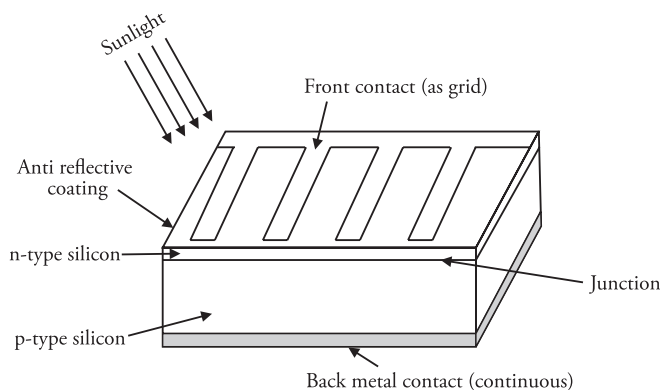


Figure 1.22 Schematic diagram of a solar cell

Wind Energy

Wind energy is the energy generated by harnessing the energy of winds, usually by windmills.

Winds are caused by the uneven heating and cooling of the earth's surface and by earth's rotation. Heating and cooling of atmosphere generates convection current and thus generates winds. Winds are also caused due to the natural movement of air across land and sea.

Basic Technology

The linear kinetic energy of the wind is transformed into rotational movement needed to turn an electrical turbine. A rotor having one, two or three blades is used to bring about this transformation. The rotors of the wind turbine rotate generating power. This energy generated can be harnessed in various ways:

- (a) *In Batteries* The power generated from wind turbines can be used to charge batteries which can store energy in the form of chemical energy for later use.
- (b) *Heating* The power generated can be used to heat water either by passing power through a resistance or by churning water.
- (c) *Fuel cells* The generated power can be used to produce hydrogen and oxygen by the electrolysis of water. These gases can then be used to generate electricity using fuel cells.
- (d) *Wind pumps* Wind turbines can be used for producing mechanical power for pumping water. These are called wind pumps and the pumped water can be used for irrigation, domestic water supply or can be stored in large overhead tanks for later use.
- (e) *Integration with the grid* The power output of wind turbine can be integrated with the electric grid to be utilised later during the no wind periods.

Advantages and Disadvantages of Wind Energy

Wind energy, like solar energy is clean energy. The operation and maintenance cost of windmill is low. However, the initial installation cost is high.

The demerits include the uncertainty of the strength of wind, high noise created by the moving windmill; moreover it also affects scenic beauty of the natural landscape adversely. Sometimes birds are killed by flying into the rotors.

Energy from Water/Hydroenergy

It is the energy generated from flowing and falling water. Water is stored in dams built across flowing rivers. This raises the water level thereby increasing its potential energy or hydraulic head. The water falls on hydraulic turbines which convert pressure and kinetic energy of water into rotational kinetic energy. The rotating shaft of the turbine drives the generator which transforms mechanical energy into electrical energy. Electrical energy is then transmitted using transmission lines (Fig 1.23).

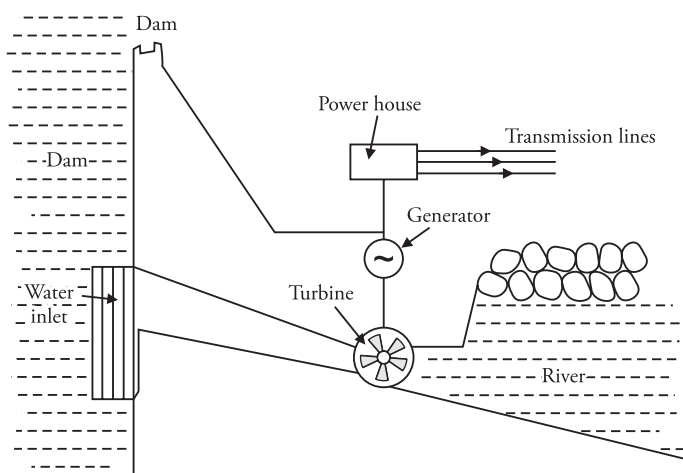


Figure 1.23 Schematic diagram of hydroelectric power plant

Advantages and disadvantages of hydroelectricity

At present hydroelectricity is the only renewable energy resource used to generate electricity on large scale. It does not cause pollution and is more reliable than wind or solar or wave energy. However it involves building of dams which is very expensive and leads to submerging of low lying areas, loss of forest and agricultural land and the need to rehabilitate people living in the submerged zones. Moreover the impounded water also increases the seismicity of the region.

Tidal Energy

All celestial bodies in the universe attract each other. The sun and the moon exert gravitational pull on the earth. This causes the surface water on the earth to rise up and bulge towards the moon leading to the formation of tides. Tides are formed periodically in the oceans due to various positions of the rotating moon and sun. Tide formation brings about a water level difference in the oceans. The highest level of tidal water is known as the high tide or the flood tide and the lowest level is known as the low tide or ebb. This difference in water level of high tide and low tide is called the tidal range and it contains large amount of potential energy. Tidal ranges of about 5 m and above can be used to drive turbines coupled with generator to generate electricity.

Basic Technology

A tidal power plant consists of a reservoir or basin to hold water during high tides. A dam or dyke acts as a barrier between the sea and the reservoir /basin. The dam is provided with a series of sluice gates to permit the entry of water into the basin during high tides (Fig 1.24).

When there is high tide the water level rises and the water enters the reservoir/basin through the sluice gates. The impounded water is held there till the tide recedes creating a suitable head. The water is then released through turbines thus generating electricity. The water is released till the head falls to the minimum operating point. As the water rises again during high tide the basin is filled again thus repeating the cycle.

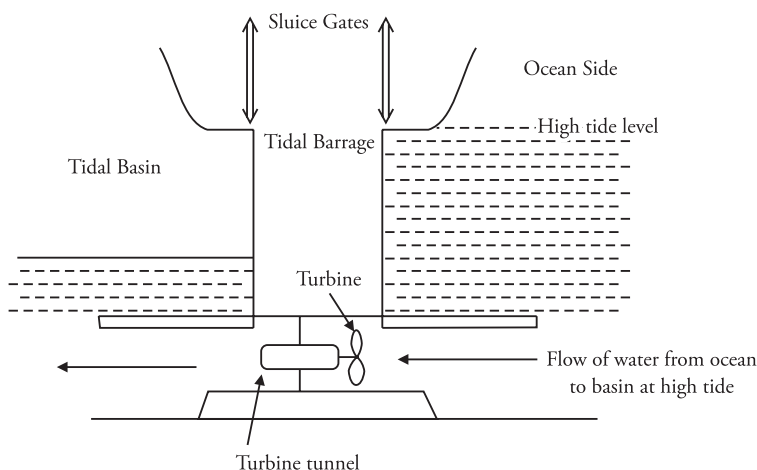


Figure 1.24 Schematic diagram of a tidal power plant

Advantages and Disadvantages

Tidal energy like any other renewable energy source does not cause pollution and is inexhaustible. However it is generated in regions far away from the load centres thereby increasing the cost of transmission.

Wave Energy

Waves originate due to the transfer of wind energy to the surface of sea water. The height and strength of waves depend upon the speed of the wind and the distance over which it interacts with water. The waves possess both kinetic and potential energy – the former due to the movement of waves and the latter due to the lifting of water mass above the sea level. Waves can rise from a height of 10 m to 100 m above the sea level. The power of waves can be harnessed to generate electricity.

Basic technology

The technology for harnessing energy from waves is different from that of tides because tides provide a much larger water head than waves do and the tides are periodic whereas waves are fluctuating. The common devices used to convert wave energy to electric energy are described below:

- (1) *Heaving float type* This device floats on the water surface and moves up and down with the vertical motion of the waves. This vertical motion is used to operate a piston of an air pump which stores energy as compressed air. The compressed air is used to generate electricity using an air turbine coupled to a generator. The floating devices are kept in place by anchoring them to the sea bed.
- (2) *Pitching type* In these devices the waves strike horizontally causing the flaps of the device to swing back and forth. This motion is used to power a hydraulic pump coupled to a generator to generate electricity.
- (3) *Heaving and pitching float type* In these types of devices both horizontal and vertical wave motions are used to generate power. These motions are converted into unidirectional motion with the help of ratchet and wheel arrangement. This motion then drives floating and stationary generators.

Although wave energy has a great potential but the technology is nascent and requires research to enable us to generate electricity on a commercial scale.

Energy from Biomass

Biomass is one of the oldest sources of energy. Wood has been used to generate energy from times immemorial. Today many sources of biomass like plants, agricultural waste, organic waste from industries and cities, municipal solid waste, forest residues are used to generate energy. Dedicated energy crops such as fast growing trees and grasses can be used as sustainable long term source of biomass. Oil obtained from petro plants is also used as source of bioenergy.

Biomass can be converted into energy by three basic technologies:

- (1) Incineration (2) Thermochemical process (3) Biochemical process
- (1) *Incineration* Incineration means the direct combustion of biomass in furnaces called incinerators. Biomass such as waste wood, agricultural waste products, waste from food industry, municipal solid waste is burnt and the heat thus produced can be used either for space heating or cooking or to generate steam in boiler to run turbine coupled to a generator

to produce electricity. A schematic diagram of generating electricity from biomass by incineration is shown in Fig 1.25.

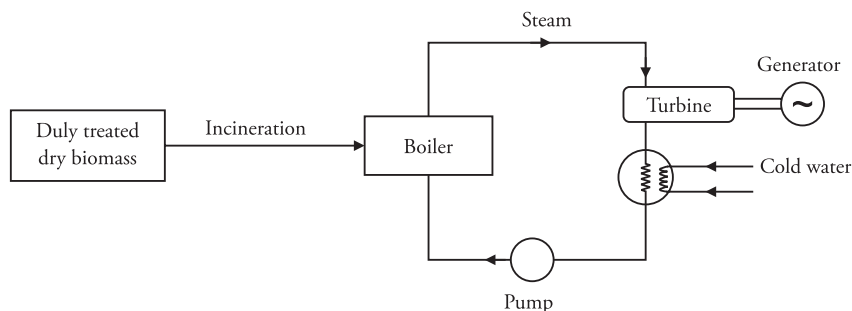


Figure 1.25 Schematic diagram of generating electricity from biomass by incineration

- (2) **Thermochemical** Thermochemical process involves the conversion of solid biomass in either absence of air or limited supply of air. The process is called *pyrolysis* or *gasification* and can be used to process solid fuels like rubber and plastic which cannot be processed by other methods. Gasification is carried out in a gasifier and it converts the biomass either into a mixture of gases such as H_2 , CO , CO_2 , CH_4 and N_2 (mainly producer gas) or liquid in the form of oil. The end product depends upon the feedstock and the temperature and pressure conditions employed. Gaseous products are generally formed when pyrolysis is carried out above $1000^\circ C$ and liquid products are formed at low temperature ($250\text{--}450^\circ C$) and high pressure (270 atm). Fig 1.26 gives a schematic diagram of gasification/pyrolysis process for generation of electricity.

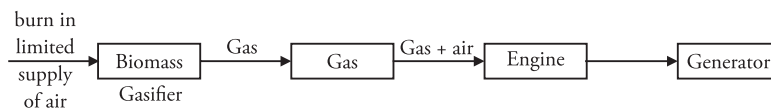
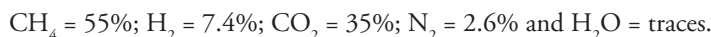


Figure 1.26 Schematic diagram of generating electricity by pyrolysis (Thermochemical process)

- (3) **Biochemical** This method involves the anaerobic digestion of biological matter. Organic matter, animal dung, poultry waste, vegetable matter, human excreta, plant waste, etc. are subjected to the action of microorganisms in closed tank in the absence of oxygen (anaerobic conditions). The organic matter undergoes degradation and a gas rich in methane is evolved. This gas is collected and can be used in kitchens as fuel. It is highly inflammable and is called biogas or *gobar* gas. Its approximate composition is:



Its average gross calorific value is 5300 kcal/m^3

Manufacture A biogas plant consists of an underground tank called the digester and a gas holder above the ground. The digester is made up of bricks masonry wall in cement mortar. Two small tanks are constructed on the ground on either sides of the digester. In one tank the dung and water are mixed and fed into the digester by a sloping pipe. Another pipe serves as an outlet pipe through which the digested slurry is removed and collected in the second tank. A gas holder made up of steel is placed on top of the digester and it helps to collect the gas thus produced. It can be fixed or floating type (Fig. 1.27).

Working A mixture of animal dung and water in equal proportion (slurry) is fed into the digester with the help of the inlet pipe. The slurry is filled till the top of the digester. It undergoes fermentation in about 50 to 60 days, and the biogas starts accumulating in the dome-shaped gas holder. The pressure of the gas pushes the digested slurry out, which is collected in another tank and is used as a manure.

Uses Biogas is a clean fuel and is used for cooking and as an illuminant in rural areas. The spent slurry is a very useful fertilizer and has 43% more strength than dung used directly as manure.

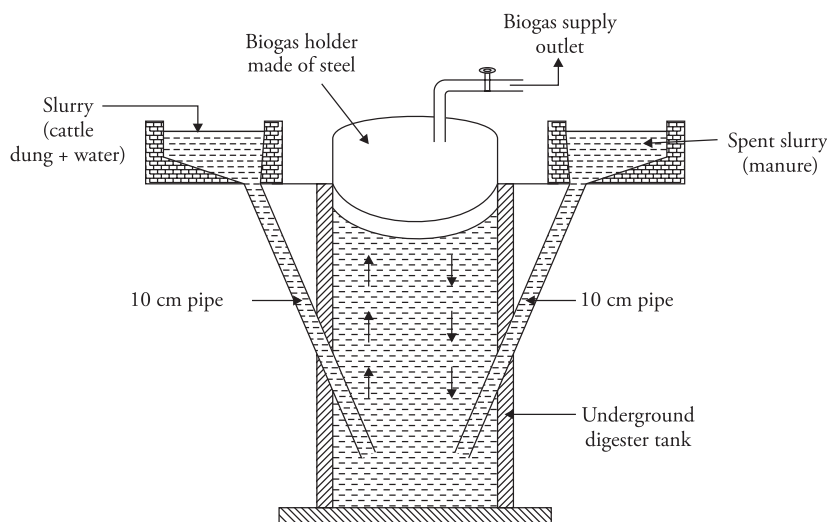


Figure 1.27 Floating gas holder type biogas plant

Geothermal Energy

Geothermal energy is the energy which lies embedded within the earth's crust. The temperature of earth increases with depth below the surface. All the heat stored in the earth's crust as thermal energy constitutes an inexhaustible source of energy termed as geothermal energy.

Hot molten rock called 'magma' is present at a depth of 25–40 km below the earth's surface. This molten magma is sometimes pushed up towards the surface resulting in volcanic eruption. When ground water comes in contact with magma it gets heated. In some places, the steam or hot water comes out of ground naturally through cracks in the form of natural geysers; this hot geothermal water or steam is used to operate turbines to generate electricity.

Geothermal energy is large enough to meet the energy requirement for nearly 3,50,000 years but the limitation is the technology to harness it economically. Although unlike solar and wind energy, geothermal energy is available all the time and does not depend on the weather conditions; however there are certain disadvantages as well. Continuous extraction of heated water from the ground can lead to subsidence of land in that area. Moreover geothermal water is accompanied by dissolved gases that lead to air pollution.

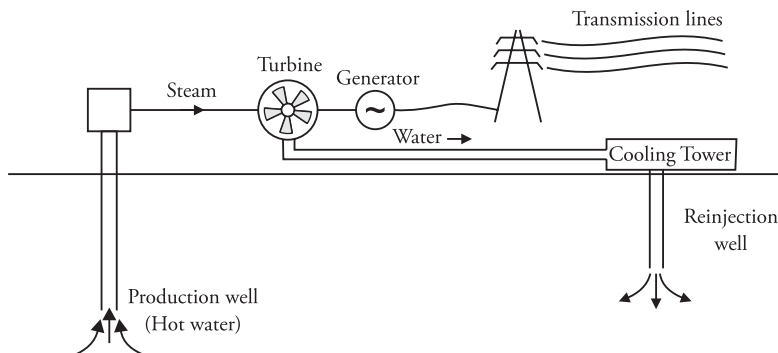


Figure 1.28 Schematic diagram of a geothermal power plant

Ocean Thermal Energy Conversion

A temperature difference exists between the surface and deep sea water. This temperature difference between the surface and deep sea water is utilised to generate electricity.

This process is based on the thermodynamic principle which states that if a heat source (warm ocean surface water) is available at a higher temperature and a heat sink (deep colder water) at a lower temperature then it is possible to utilise the temperature difference to convert part of the heat from the source into mechanical energy by connecting the turbine to a generator. The residual heat is discharged to the sink which is at a lower temperature.

A minimum temperature difference of 20 °C is necessary to bring about useful energy conversion.

Basic Technology

Steam is required to move the turbine to generate electricity. In an OTEC plant this steam comes either by evaporating a low boiling liquid (called working fluid) or by the evaporation of sea water. Depending on the technique used, the OTEC plants can operate in the following ways:

- (1) Closed cycle or Anderson cycle OTEC plant
- (2) Open cycle or Claude cycle OTEC plant
- (3) Hybrid OTEC plant

Closed cycle OTEC plant In a closed cycle OTEC plant the working fluid, a low boiling point liquid (refrigerant) such as ammonia, freon or propane is evaporated using the warm surface water of the sea. The vapours thus formed give their energy to the turbine which is coupled with a

generator to produce electricity. These vapours are then condensed in a condenser using cold water from deep sea (Fig 1.29).

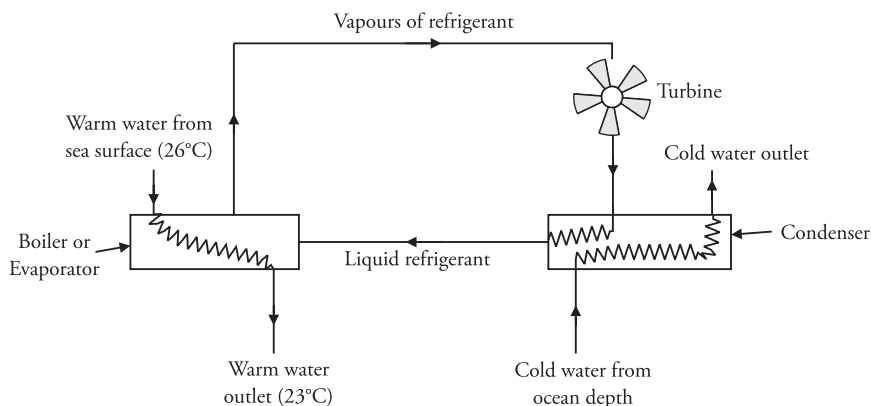


Figure 1.29 Closed cycle OTEC plant

Open cycle OTEC plant In case of open cycle OTEC plant the warm surface water of the sea/ocean is evaporated at a very low pressure in a flash evaporator. The flash evaporator maintained at partial vacuum enables water to boil at a low temperature. The vapours thus formed move the turbine thereby generating electricity. The vapours are then cooled by cold water drawn from the ocean depths (Fig 1.30). The condensate is desalinated fresh water that can be used as potable water and for irrigation.

However open cycle is more expensive as it requires expensive degassing and vacuum pumps.

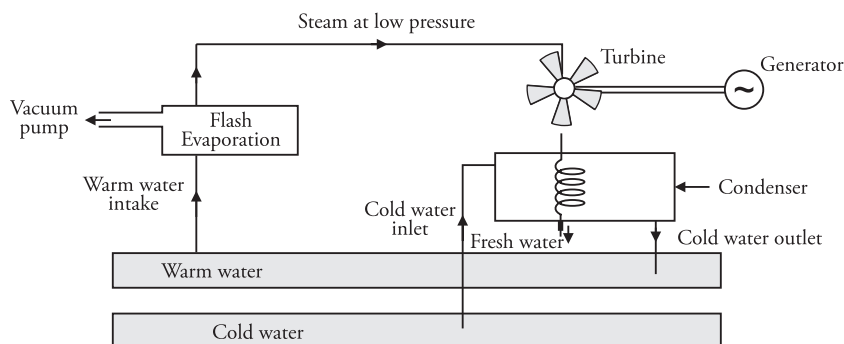


Figure 1.30 Open cycle OTEC plant

Hybrid OTEC plant The open OTEC cycle produces potable water whereas the closed cycle has larger potential for electricity generation. The hybrid OTEC cycle combines the two and produces potable water like the open cycle and has large power generation potential like the closed cycle.

Like the open cycle the warm surface sea water is evaporated at a very low pressure in a flash evaporator and this low pressure steam is used to vaporise the low boiling point fluid (working fluid) such as ammonia. These vapors of the low boiling point fluid drive the turbine to generate electricity and the steam is condensed to yield potable water.

Advantages and disadvantages

The OTEC plant supplies energy steadily without being affected by weather. However the installation is expensive and may cause adverse environmental impact on the aquatic ecosystem.

Hydrogen Energy

Hydrogen is often considered as a non-conventional fuel because it is produced from water which can be split into gaseous hydrogen and oxygen by an electrical process called electrolysis. Hydrogen can also be produced from natural gas and biomass resources.

Hydrogen is considered as a renewable fuel because the earth's supply of water is unlimited. Hydrogen gas can be used like natural gas. It can be burnt to heat buildings, cook food and produce electricity in power plants. Hydrogen can also be used as fuel in automobiles, in a jet aircraft (liquid hydrogen). Hydrogen can also be used in fuel cell devices that combine hydrogen and oxygen to produce electricity (*fuel cells are discussed in detail in Chapter sixteen on Electrochemistry section 16.18*).

Advantages and disadvantages

It is a renewable and clean source of energy as hydrogen burns to yield water only and in some cases very small amounts of nitrogen oxides may be formed. However hydrogen gas is highly inflammable and the production, transportation and storage of hydrogen requires huge capital investment.

Advantages and Disadvantages of Renewable Energy

Advantages of Renewable Energy

1. One of the major advantages of renewable energy is that, as it is renewable, it is sustainable and will therefore never run out.
2. Renewable energy facilities require less maintenance than traditional generators.
3. As their fuel is derived from natural and available sources, the cost of operation is less.
4. Renewable energy produces little or no waste products such as carbon dioxide or other chemical pollutants, so it has minimal impact on the environment.

Disadvantages of Renewable Energy

1. It is difficult to generate the quantities of electricity as large as that produced by traditional fossil fuel generators.

2. It can be unpredictable and inconsistent. The supply from renewable sources is not reliable, as it relies on weather for its source of power. Hydro generators need rain to fill dams, wind turbine needs wind to turn the blades and solar collectors need clear skies and sunshine to collect heat and generate electricity.
3. The current cost of renewable energy technology is far in excess of traditional energy. This is because it is a new technology and as such has extremely large capital cost.

Energy Storage

Energy storage is important so that excess energy can be stored to be used later. Moreover energy from sources like sun and wind is produced intermittently, hence storage is essential so that the stored energy can be used when there is no electricity generation. Sometimes energy is generated at a place which is far away from its consumption site (ocean energy, energy from waves, tides, geothermal energy, etc.). In these cases also energy storage becomes essential.

Energy can be stored in various ways. Some of them are discussed below

- (1) **Mechanical Energy Storage** Excess energy is stored as mechanical energy.
 - (a) *Pumped Storage* In this method the electrical power in excess of immediate demand is used to pump water from a lake, river or reservoir at a lower level to a reservoir at higher level. During the demand period this stored water is allowed to fall on a hydraulic turbine which drives an electric generator to generate electricity.
 - (b) *Compressed air storage* In this system, the excess electrical energy is used to compress air which is stored in a reservoir to be used later in a gas turbine to generate electricity.
- (2) **Chemical Storage** A storage battery receives excess electricity and stores it in the form of chemical energy. This energy can be retrieved to give electrical energy later (for details refer electrochemical cells chapter 16).
- (3) **Thermal Storage** In this type of storage, the temperature of storage material rises when energy is absorbed and drops when energy is withdrawn.

1.31 Nuclear Fuels

Nuclear fuels produce energy by nuclear reaction in which the number of protons and neutrons in the nucleus are altered resulting in the formation of a new nucleus of another atom with a different atomic number and mass number. Large amount of energy is released during this process and the energy released by a nuclear reaction is million times more than the energy produced by a chemical reaction. For example fission of 1 kg uranium (discussed later in chapter) releases nearly 2×10^7 kWh (kilowatt hour) energy which is nearly equal to burning 2000 tons of high grade coal or 3000 tons of average grade coal.

Mass energy equivalence

In nuclear reactions the mass of products is generally less than the mass of the reactants. This mass difference is converted into energy and is determined by using the Einsteins mass energy equation.

$$E = mc^2$$

where E = Energy equivalent of mass m and c is the velocity of light.

For a charge of 1amu (atomic mass unit), the corresponding energy change is

$$\begin{aligned} 1 \text{ amu} &= 1/12^{\text{th}} \text{ of the mass of a carbon atom} \\ &= \frac{1}{12} \times \frac{12}{6.023 \times 10^{23}} = 1.6606 \times 10^{-24} \text{ g} = 1.6606 \times 10^{-27} \text{ kg} \end{aligned}$$

Taking the value of c = 2.9979×10^8 m/s we have

$$\begin{aligned} E &= 1.6606 \times 10^{-27} \text{ kg} \times (2.9979 \times 10^8 \text{ m/s})^2 = 1.4924 \times 10^{-10} \text{ J} \\ &= 1.4924 \times 10^{-10} \text{ J} \times \frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}} \\ &= 931 \times 10^6 \text{ eV} = 931 \text{ MeV} \end{aligned}$$

Hence a mass of 1 amu is equivalent of 931 MeV of energy.

Mass defect (Δm) and binding energy

The masses of various atomic nuclei are invariably found to be less than the sum of the masses of the corresponding nucleons i.e sum of masses of protons and neutrons in the nucleus. This difference in mass is termed as 'mass defect' and this loss of mass appears as energy given by the Einsteins relation $E = mc^2$

This can be illustrated as follows:

Measured mass of helium atom = 4.0026 amu

Calculated mass of helium atom = mass of two protons + mass of two neutrons

$$\begin{aligned} &= 2 \times 1.00815 + 2 \times 1.00899 \\ &= 2.0163 + 2.01798 \\ &= 4.03428 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{Mass defect of helium } \Delta m &= 4.03428 - 4.0026 \\ &= 0.03168 \text{ amu} \end{aligned}$$

This mass (0.03168 amu) will be converted into energy and it is this energy that binds the nucleons together in the nucleus. It is termed as the *binding energy*. The binding energy is expressed in million electron volts (MeV) and it is also the energy needed to break the nucleus into its constituent nucleons ($1\text{MeV} = 1.602 \times 10^{-6}$ ergs).

Mathematically binding energy (BE) and mass defect (Δm) are related as follows:

$$BE = 931 \times \Delta m$$

Binding energy per nucleon is given by

$$\text{Binding energy per nucleon} = \frac{\text{Binding energy of nucleons}}{\text{number of protons} + \text{number of neutrons}}$$

For He atom binding energy will be

$$\Delta m \times 931 = 0.03168 \times 931 = 29.4948 \text{ MeV}$$

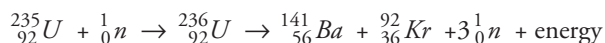
$$\text{Binding energy per nucleon} = \frac{29.49408}{4} = 7.37352 \text{ MeV}$$

(since helium atom has two protons and two neutrons)

It is important to note that greater the binding energy more is the stability of the nucleus.

Type of nuclear reactions

Nuclear fission It is the process of splitting of heavy nuclei such as ^{235}U , ^{233}U or ^{239}Pu (by bombarding with neutrons) into lighter fractions called 'fission fragments' accompanied by the simultaneous liberation of two or three fresh neutrons and huge amount of energy



Energy is released due to the conversion of mass into energy for the above reaction :

Initial mass

$$^{235}_{92}\text{U} = 235.0439 \text{ amu}$$

$${}^1_0\text{n} = 1.0087 \text{ amu}$$

$$236.0526 \text{ amu}$$

Final mass

$$^{141}_{56}\text{Ba} = 140.9139 \text{ amu}$$

$$^{92}_{36}\text{Kr} = 91.8973 \text{ amu}$$

$$3{}^1_0\text{n} = 3.0261 \text{ amu}$$

$$235.8373 \text{ amu}$$

\therefore mass defect is 0.2153 amu which is equivalent to $0.2153 \times 931 \text{ MeV} = 200.44 \text{ MeV}$

This is the energy released by the fission of one $^{235}_{92}\text{U}$

Nuclear Chain Reaction

In the reaction discussed above fission of one nucleus produces three neutrons. It may be added here that U-235 is known to split in 30 different ways. These three neutrons will cause fission of three more $^{235}_{92}\text{U}$ atoms producing nine neutrons which bombard nine $^{235}_{92}\text{U}$ nuclei producing twenty seven neutrons and so on

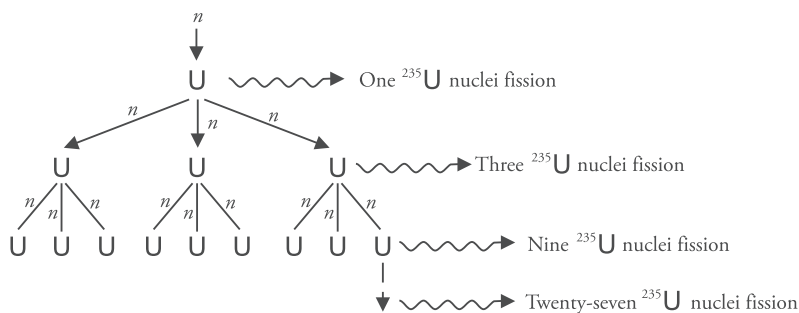


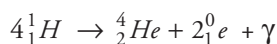
Figure 1.31 Nuclear chain reaction

Thus a chain reaction is set up wherein huge amount of energy is released. It is to be noted here that all the neutrons produced during fission do not strike a nucleus to cause further fission. Some of them escape into the air and are lost. If too many neutrons escape into the air then a chain reaction cannot be set up. To sustain a chain reaction the size of Uranium-235 must be larger than a 'critical size'. Atom bomb is based on the principle of nuclear fission.

The chain reaction can be controlled by absorbing the neutrons so that on an average one neutron is available for further fission. This controlled chain reaction forms the basis of nuclear reactor.

Nuclear Fusion

It is the process of fusion of two or more lighter nuclei to give a heavier nuclei with simultaneous release of energy. The principle source of solar energy is the fusion of hydrogen nuclei to produce helium nuclei. The reaction occurs as follows:



The mass of $4 {}_1^1\text{H} = 4 \times 1.00813 = 4.03252$ amu

Mass of ${}_2^4\text{He} = 4.00389$ amu

The mass defect $\Delta m = 4.03252 - 4.00389 = 0.02863$ amu

This is equivalent to $0.02863 \times 931 = 26.6545$ MeV energy which is released during the fusion process.

However, it is very difficult to achieve the fusion of two or more nuclei, because as these nuclei approach each other they have to overcome strong electrostatic force of repulsion. Fusion reaction takes place at extremely high temperature of the order of 100 million degree Celsius. Hence fusion reactions are termed as thermonuclear reactions.

Hydrogen bomb works on the principle of nuclear fusion where the initial high temperature required to trigger the fusion reaction is obtained by fission reaction or an atom bomb.

Table 1.7 Difference between nuclear fission and fusion

S. N	Nuclear fission	Nuclear fusion
1.	It is the process of breaking of heavier nuclei into lighter nuclei	Fusion process involves the union of two or more lighter nuclei to form a heavier nucleus
2.	The neutrons released initiate further reaction resulting in a chain reaction	Nuclear fusion is never as chain reaction
3.	Fission reaction occurs spontaneously at ordinary temperature	Fusion reaction is triggered by extremely high temperature of the order of 100 million degree Celsius
4.	Nuclear fission can be performed under controlled conditions	Nuclear fusion cannot be controlled
5.	Nuclear fission leads to the production of radioactive isotopes	Radioactive isotopes are not formed in the fusion process
6.	To sustain a chain reaction in fission process the size of fissionable material should be greater than a minimum size called the 'controlled mass'	There is no such size limit for a fusion process to sustain
7.	Eg. Atom bomb	Eg. Hydrogen bomb

Nuclear reactor or Atomic Pile

In a nuclear reactor the nuclear fission is carried out at a controlled rate to produce energy which is used to generate electricity. The chief components of a nuclear reactor are as follows:

1. **Reactor core:** It is the principle component of the reactor where the fissionable material is located and controlled fission reaction occurs, liberating huge amount of energy. The reaction core consists of an assembly of fuel element, control rods, coolant and moderator.

(a) **Fuel element:** The fissionable material used in the nuclear reactor may be –

- Natural uranium containing 0.71% of fissile ^{235}U isotope
- Enriched uranium containing higher % of ^{235}U
- ^{239}Pu obtained from ^{238}U
- ^{232}Th is which fissile ^{233}U is mixed

The fuel material in the form of pellets or rods is shielded by placing it in stainless steel tubes or zirconium aluminium alloy.

- (b) **Moderator:** It moderates or reduces the kinetic energy of fast fission neutrons (from 1-2 MeV to nearly 0.025 eV) within fraction of a second. These slow neutrons maintain the fission chain reaction in the nuclear reactor. Water, heavy water (D_2O), graphite and beryllium are commonly used as moderators.

Heavy water (D_2O) is an excellent moderator as it slows down neutrons efficiently and can also be used as a coolant. However the major disadvantage of D_2O is its low boiling point and high cost (about 500/kg)

Beryllium: Although cheap it is not a good moderator as it breaks when brought in contact with oxygen, air and carbondioxide at high temperatures..

- (c) *Coolant*: The function of the coolant is to remove the intense heat generated in the core of the reactor. The coolant generally used are : ordinary water, heavy water, liquid metals like Na or K, organic compounds such as benzene and polyphenyls(eg. diphenyls and terphenyls), gases like CO_2 , H_2 , He and air.

The coolant absorbs the heat which is then transferred to the working fluid to generate steam which is then used in a turbo- generator system. Sometimes the heat generated in the core is directly used to generate steam.

An ideal coolant should have high specific heat capacity, high thermal conductivity, low neutron absorption cross section and should be stable to heat and radiation.

- (d) *Control rods*: These rods made up of material like cadmium or boron are used to control the fission process by absorbing neutrons. These rods have high neutron absorption capacity and absorb more neutrons when pushed inside the core of the reactor and reduce reactivity; they absorb less neutrons when pulled out and the reaction will be fast.

Hence control rods help to maintain steady supply of power and are used to shut down the reactor during normal operation or during emergency.

2. *Reflectors*: The reactor core is surrounded with reflector with the purpose of reflecting the neutrons that leak out from the core. In thermal reactors the same material (viz D_2O , graphite, Be or H_2O) used as moderator is also used as a reflector. However it is important that the reflector should have low absorption and high reflection for neutrons. The reflector helps to increase the average power output for a given quantity of the fuel.
3. *Pressure vessel*: It encloses the core and the reflector and is designed to withstand a pressure up to 300 kg/cm^2 . It is provided with holes at the top for the control rods and also provides passage for the entry and exit of the coolant.
4. *Protective shield*: Although the shield has nothing to do with the working of the nuclear reactor but still it is an important component as it absorbs the radiations coming out of the reactor. If these radiations leak into the atmosphere they will be harmful for biotic and abiotic environment. Two type of shields are generally employed
 - (i) *Thermal shield*: It is 50-60 cm thick iron or steel covering around the reactor core. It became heated by absorbing gamma rays. It prevents the walls of pressure vessel from becoming hot and is cooled by circulating water.
 - (ii) *Biological shield*: It is several feet thick layer of concrete surrounding the thermal shield; It absorbs γ rays and neutrons coming out from the thermal shield.
5. *Heat exchangers*: They transfer the heat liberated from reactor core to boil water and produce steam.
6. *Turbine*: The steam generated is used to operate turbine and produce electricity.

Light water nuclear power plant

As indicated by the name light water reactors use normal water both as a coolant and as neutron moderator. Slightly enriched uranium or more specifically uranium oxide UO_2 (2.5–4%) stacked inside as a fuel cladding sealed from outside constitute the fuel rod or fuel pin which produces energy by controlled fission process.

The fission reaction is controlled by inserting or removing the boron-10 control rods in the places between the fuel rods.

Depending upon how the heat generated in the fission process is utilised to produce energy the light water reactors are further of two types:

In *boiling water reactors* the heat produced by fission is absorbed by the coolant (light water) which generates steam directly by boiling water in the reaction core. This steam drives the turbine and generates electricity. On the other hand in *pressurised water reactors* the heated coolant (light water) transfers the energy to sea water (in a secondary loop via a heat exchanger) which is converted into steam which then drives the turbine generating electricity. Some important nuclear power plant in India are: Tarapur near Mumbai established in year 1960, and another set up at Narora in Uttar Pradesh and Rawatbhata in Rajasthan.

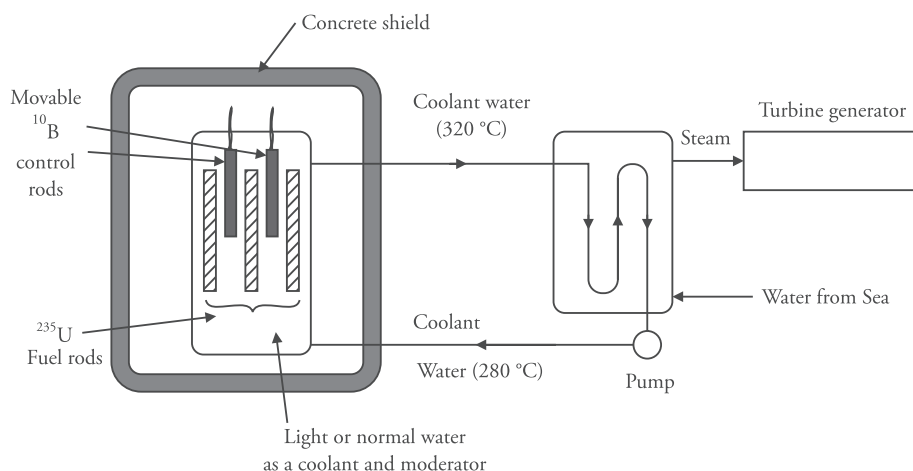
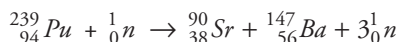
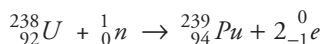


Figure 1.32 Light water nuclear power plant

Breeder reactor

These reactors breed fissile materials. We have seen earlier that a nuclear reactor uses ^{235}U to produce electricity. However natural uranium contains only 0.7% of fissile ^{235}U and majority of uranium consists of non-fissile ^{238}U isotope. A breeder reactor generates its own fuel by converting non fissile ^{238}U and ^{232}Th into fissile material ^{239}Pu and ^{233}U respectively. The ^{235}U core is covered with a layer or blanket of ^{238}U . The neutrons released by ^{235}U are absorbed by ^{238}U which is then converted to ^{239}Pu . It undergoes a chain reaction producing more neutrons and energy.



The above reaction consumes two neutrons and produces three. This extra neutron converts more uranium into plutonium. Therefore reactor produces or breeds more new fuel than it consumes and hence its name.

Summary

- Fuel is a combustible substance containing carbon as the major constituent. On proper combustion it gives large amount of heat.
- Fuel can be: (i) primary or natural or (ii) secondary or derived.
- Primary fuels are found in nature as such, for example, wood, peat, coal and petroleum.
- Secondary fuels are derived from primary fuels, for example, charcoal, coke, kerosene, coal gas, etc.
- On the basis of aggregation fuels are classified as solid fuels, liquid fuels and gaseous fuels.
- Solid fuels are wood, coal, charcoal, coke, etc.
- Coal can be converted into coke by the process of carbonisation.
- There are two types of carbonisation of coal: (i) low-temperature carbonisation (ii) high-temperature carbonisation.
- Metallurgical coke can be obtained by two methods: (i) Beehive oven and (ii) Otto Hoffman's by-product oven method.
- The quality of coal is analysed by two methods: proximate analysis and ultimate analysis.
- Proximate analysis is used to measure the amount of moisture, volatile matter, ash and fixed carbon in the coal sample.
- Ultimate or elemental analysis measures the amount of carbon, hydrogen, oxygen, nitrogen and sulphur in the coal sample.
- The amount of heat liberated on combustion of unit mass of a fuel is its calorific value.
- Calorific value of solid and non-volatile liquid fuels is measured with the help of a bomb calorimeter.
- Junkers calorimeter and Boy's calorimeter are used for the determination of calorific value of gaseous and volatile liquid fuels.
- Calorific value can be found out theoretically with the help of Dulong's formula.
- Higher or gross calorific value of a fuel is the heat liberated when a unit mass/ volume of the fuel is burnt completely and the gaseous products are cooled to room temperature.
- Net or lower calorific value is the heat liberated when a unit mass /volume of the gaseous fuel is burnt completely and the gaseous products are allowed to escape.
- Liquid fuels include petrol, kerosene, diesel, etc., all these obtained by the fractional distillation of petroleum or crude oil.

- Of all the fractions obtained the most sought after is gasoline. The higher molecular weight fractions can be converted to low molecular weight fractions (gasoline) by cracking.
- Cracking is of two types: (i) thermal and (ii) catalytic. Catalytic cracking can be fixed bed catalytic cracking or fluidised bed catalytic cracking.
- Gasoline can be synthesized by polymerisation, alkylation, Fischer Tropsch method and Bergius method.
- The ignition quality of gasoline is measured by octane number, which is a measure of its knocking property.
- Knocking is the rattling sound produced in internal combustion engine.
- The quality of gasoline can be improved by reforming, that is, by bringing about structural modifications its antiknock characteristics can be improved.
- Tetraethyl lead (TEL) and diethyl telluride $(C_2H_5)_2Te$ are added to gasoline to improve its antiknock characteristics.
- The ignition quality of diesel engine fuels is measured in terms of cetane number.
- Gaseous fuels are coal gas, oil gas, etc.
- Coal gas is obtained as a by-product of the destructive distillation of coal.
- Oil gas is obtained by the cracking of kerosene oil.
- The gases produced on combustion are called flue gases and can be analysed by the Orsat's apparatus.
- By combustion calculations the amount of air required by weight and volume can be estimated and conditions can be controlled during the combustion process.
- Non-conventional energy sources or renewable energy sources are those energy sources that can be replenished naturally like the solar energy, wind energy, energy from water, tides, oceans, geothermal energy and hydrogen energy. They are also called alternate sources of energy.
- Solar energy can be used either for heating purposes or to generate electricity directly using silicon solar cells.
- Wind energy is converted into electrical energy by using wind turbines.
- Hydroenergy is harnessed by storing water in dams and allowing water to fall on turbines. The rotating shaft of turbine moves an electric generator generating electricity.
- Electricity is obtained from tidal energy. Water during high tide is stored in tidal basin which is then used to rotate a turbine to generate electrical power.
- Energy of waves is converted into electricity using heaving float type and pitching type devices.

- Energy is obtained from biomass by incineration, pyrolysis or anaerobic digestion.
- Geothermal energy is harnessed by moving turbines using the hot geothermal water.
- The temperature difference of surface water and water at depth inside the oceans helps to generate electricity. Open, closed and hybrid OTEC plants are deployed for the purpose.
- Renewable energy is clean, does not cause pollution and is abundantly available. However it is expensive and presently only hydroenergy is being used on a very large scale.
- Energy produced by different sources can be used later by storing energy mechanically (pumped storage, compressed air storage), chemically in electrochemical cells or thermally.
- Nuclear fuels produce energy by nuclear reaction. In these reactions some of the mass of reactants (equivalent to mass defect, that is, the difference in mass of reactants and products) is converted into energy.
- Nuclear reactions are of two types : fission and fusion. In fission a large molecule is broken into smaller molecules with the release of energy and in fusion small molecules combine to give a larger molecule again with the release of huge amount of energy.
- Nuclear reactor is used to produce energy by controlling the fission reaction.
- In light water reactors normal water is used both as a coolant and as neutron moderator.
- A breeder reactor produces more fissionable material than it consumes.

Review Questions

1. Define fuel. What are the different types of fuels and how are they classified?
2. What is calorific value of a fuel? Define gross calorific value and net calorific value of a fuel and write down the relation between them.
3. What is calorific value? How can you measure the calorific value of a solid fuel with the help of a bomb calorimeter?
4. With the help of a well-labeled diagram explain the determination of calorific value of a gaseous or volatile liquid fuel using a Junkers gas calorimeter.
5. Enumerate the important characteristics of a good fuel.
6. What is proximate analysis of coal? Why is it called so? Discuss its significance.
7. What are the different types of fuels. Compare solid, liquid and gaseous fuels?
8. What is the necessity and significance of elemental analysis of coal? How can you analyse coal with the help of ultimate analysis?

9. What is carbonisation of coal? Discuss the process of carbonisation of coal.
10. What is metallurgical coke? What are the requisites of good coke used for metallurgical purpose?
11. What is the difference between low temperature and high temperature carbonisation of coal? Why is coke preferred to coal in metallurgical operations?
12. How can you manufacture metallurgical coke using a Beehive coke oven? What are the limitations of this process?
13. Describe the manufacture of metallurgical coke with the help of Otto Hofmann's oven or by-product oven method. What are its advantages over the beehive coke oven method?
14. What is petroleum? Discuss the various steps of processing of petroleum to obtain gasoline and other important fractions.
15. With the help of a neat labeled diagram describe the fractional distillation of crude petroleum and name the various products obtained.
16. What is cracking? Why is it important? Discuss the fixed bed catalytic cracking method to obtain gasoline from heavy oils. What are the limitations of the process?
17. Explain the fluidised bed catalytic cracking process for the manufacture of gasoline from heavy oils. What are the advantages of this process over the fixed bed catalytic cracking?
18. Differentiate between thermal cracking and catalytic cracking. What are the advantages of catalytic cracking over thermal cracking.
19. What is synthetic petrol? Explain the Fischer–Tropsch and Bergius process for the manufacture of the same.
20. What is knocking. How is it related to the chemical structure of the fuel. How can you reduce knocking in an internal combustion engine?
21. Explain the process of knocking in a diesel engine fuel. Define octane rating and cetane number of a fuel. How can you increase the octane number of a fuel?
22. What is reforming? Explain how reforming improves the quality of gasoline. Also explain the process of reforming with the help of a well-labeled diagram.
23. What are gaseous fuels? What are the merits and demerits of gaseous fuels over solid and liquid fuels?
24. Describe the manufacture of producer gas with the help of a neat and labeled diagram.
25. With the help of a well-labeled diagram, explain the manufacture of oil gas. What is its constitution and give the applications of oil gas?
26. Explain the manufacture of coke oven gas with the help of a well-labeled diagram.
27. How can flue gas be analysed with the help of Orsat flue gas apparatus? Discuss the significance of flue gas analysis.
28. Distinguish between the following
 - (a) Proximate and ultimate analyses.
 - (b) Coal and coke.
 - (c) Coking coals and caking coals.

- (d) Octane number and cetane number.
 - (e) Thermal and catalytic cracking.
29. Justify the need of developing the non-conventional sources of energy. Describe the various non conventional sources of energy.
 30. How is wind energy used for the generation of electric power? Discuss the merits and limitations of wind energy.
 31. How can you generate electricity from water? Explain with the help of a schematic diagram.
 32. What are tides? With the help of a well labeled diagram explain the basic technology used to generate electricity from tides. What are the limitations of this process?
 33. What is biomass? Explain the various methods of obtaining power from biomass.
 34. What is geothermal energy? How is it used to generate electrical power? Discuss its merits and limitations.
 35. Write short notes on:
 - (i) Solar water heating
 - (ii) Solar cooking
 - (iii) Solar lighting
 - (iv) Solar ponds
 36. How can you obtain electricity from solar energy? Explain the principle and working of a solar cell.
 37. How can you harness the energy of waves? What is the basic difference between energy from waves and that from tides? Discuss the technology used to obtain energy from waves. What are its limitations?
 38. How can you use the temperature difference of surface and deep ocean waters to obtain energy? Explain the open and closed cycle to convert the thermal energy of the ocean into electricity.
 39. What is nuclear fission. With the help of a neat and labeled diagram explain how nuclear fission can be controlled to produce energy.
 40. With the help of a neat and labeled diagram explain the principle and working of a light water nuclear power plant.

Multiple Choice Questions

1. A good fuel has
 - (a) Moderate ignition temperature and high calorific value
 - (b) High ignition temperature and high calorific value
 - (c) Low ignition temperature and low calorific value
 - (d) Low ignition temperature and high calorific value

2. The total quantity of heat liberated when a unit mass (or volume) of a fuel is burnt completely is called its
 - (a) Heat value
 - (b) Calorific value
 - (c) Burning value
 - (d) Combustion value
3. Calorific value of a solid or non-volatile liquid fuel is found with the help of
 - (a) Junkers calorimeter
 - (b) Bomb calorimeter
 - (c) Boys calorimeter
 - (d) Orsat apparatus
4. On the basis of its carbon contents and contents of moisture and volatile matter the best quality coal is
 - (a) Peat
 - (b) Lignite
 - (c) Bituminous
 - (d) Anthracite
5. Ultimate analysis of coal is used to determine
 - (a) Percentage of carbon and hydrogen
 - (b) Percentage of sulphur
 - (c) Percentage of nitrogen
 - (d) All of the above
6. The following can be estimated using the proximate analysis of coal
 - (a) Percentage of moisture
 - (b) Percentage of volatile matter
 - (c) Percentage of ash
 - (d) All of the above
7. Which of the following by-products is not recovered in the Otto Hoffman's by-product coke oven method
 - (a) LPG
 - (b) Benzene
 - (c) Naphthalene
 - (d) Ammoniacal liquor
8. The process of breaking bigger hydrocarbons into simpler low boiling point fractions is called
 - (a) Reforming
 - (b) Cracking
 - (c) Refining
 - (d) Knocking
9. Synthetic petrol can be obtained by
 - (a) Polymerisation
 - (b) Fischer–Tropsch method
 - (c) Bergius process
 - (d) All of the above
10. The process of bringing structural modifications in straight run gasoline to improve its antiknock characteristics is termed as
 - (a) Cracking
 - (b) Refining
 - (c) Reforming
 - (d) Knocking
11. Junkers calorimeter is used to determine the calorific value of a
 - (a) Gaseous fuel
 - (b) Solid fuel
 - (c) Liquid fuel
 - (d) None of the above
12. The ignition characteristics of diesel are expressed in terms of
 - (a) Octane number
 - (b) Cetane number
 - (c) Viscosity
 - (d) Flash and fire point

13. The addition of TEL to gasoline
 - (a) Increases the viscosity of gasoline
 - (b) Increases the rate of combustion of gasoline
 - (c) Increases the octane number of gasoline
 - (d) Decreases the octane number of gasoline
14. Following compounds have been arbitrarily assigned an octane number of zero and hundred, respectively
 - (a) n-heptane and isooctane
 - (b) n-octane and isoheptane
 - (c) Isooctane and n-heptane
 - (d) n-hexadecane and 2-methylnaphthalene
15. The cetane number of high-speed diesel, medium-speed diesel and low-speed diesel are nearly
 - (a) 40, 30 and 20, respectively
 - (b) 45, 35 and 25, respectively
 - (c) 50, 40 and 30, respectively
 - (d) 25, 15 and 5, respectively
16. Oil gas is obtained by the cracking of
 - (a) Diesel oil
 - (b) Petrol
 - (c) Kerosene oil
 - (d) Heavy oil
17. Producer gas is a mixture of
 - (a) $\text{CO} + \text{N}_2$
 - (b) $\text{CO} + \text{H}_2$
 - (c) $\text{CO} + \text{CO}_2$
 - (d) $\text{CO} + \text{O}_2$
18. The gas named as 'blue gas' is
 - (a) Producer gas
 - (b) Water gas
 - (c) CNG
 - (d) LPG
19. The gases analysed by Orsat flue gas apparatus are
 - (a) SO_2 , O_2 , CO_2 , H_2O vapours
 - (b) Cl_2 , N_2 , O_2 , SO_2
 - (c) SO_2 , CO_2 , N_2 , O_2
 - (d) CO_2 , O_2 , CO and N_2
20. Arrange n-heptane, isooctane and naphthalene in increasing order of their knocking tendency
 - (a) Naphthalene < isooctane < n-heptane
 - (b) Isooctane < n-heptane < naphthalene
 - (c) n-heptane < naphthalene < isooctane
 - (d) Naphthalene < n-heptane < isooctane
21. The catalyst used for the cracking of heavy oil is
 - (a) Ni or Sn oleate
 - (b) $\text{Al}_2\text{O}_3 + \text{ZrO}_2 + \text{clay}$
 - (c) $\text{Co} + \text{Th} + \text{MgO} + \text{keiselguhr}$
 - (d) $\text{Pt} - \text{Al}_2\text{O}_3$
22. Power alcohol is a mixture of
 - (a) Petrol + ethyl alcohol
 - (b) Diesel + ethyl alcohol
 - (c) Petrol + methyl alcohol
 - (d) Diesel + methyl alcohol

23. Which of the following is not a renewable source of energy
(a) Solar energy (b) Wind energy
(c) Petrol (d) Energy from hydrogen.
24. Coke is preferred to coal in metallurgical process because of
(a) High strength and high porosity
(b) Less sulphur content and low ash
(c) Burns with a short flame
(d) All of the above
25. The lowest boiling fraction of crude oil is
(a) Petroleum ether (b) Kerosene oil
(c) Diesel oil (d) Gasoline or petrol
26. Presently which of the following renewable energy sources is exploited the most for power generation
(a) Solar Energy (b) Hydroenergy
(c) Wind Energy (d) Geothermal Energy
27. Which of the following is a non-conventional energy source
(a) Coal (b) Petrol
(c) Diesel (d) Biomass
28. Solar energy can be used for
(a) Heating water (b) Cooking food
(c) Generating electricity (d) All the above
29. Cells commonly employed to convert solar energy to electricity are
(a) Photovoltaic cells (b) Fuel cells
(c) Secondary cells (d) Reserve batteries
30. The minimum water head essential for electricity generation from tides is
(a) 1–2 m (b) 2–3 m
(c) 3–4 m (d) more than 5 m
31. Energy generated by utilising the temperature difference in the earth's interior is called the
(a) Geothermal energy (b) Hydrogen energy
(c) Tidal and wave energy (d) Ocean thermal energy
32. Which of the following is not a fossil fuel
(a) Biomass (b) Coal
(c) Kerosene (d) Petrol
33. Material most commonly used in a photovoltaic cell is
(a) Hydrogen (b) Silicon
(c) Tellurium (d) Antimony

Solutions

1 (a)	2 (b)	3 (b)	4 (d)	5 (d)	6 (d)	7 (a)	8 (b)	9 (d)	10 (c)
11 (a)	12 (b)	13 (c)	14 (a)	15 (b)	16 (c)	17 (a)	18 (b)	19 (d)	20 (a)
21 (b)	22 (a)	23 (c)	24 (d)	25 (a)	26 (b)	27 (d)	28 (d)	29 (a)	30 (d)
31 (a)	32 (a)	33 (b)							

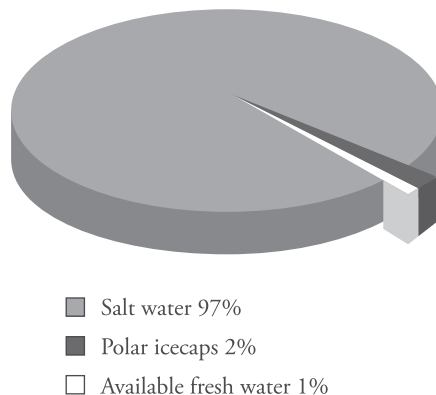
Chapter 2

WATER

2.1 Introduction

Water is the most precious, wonderful and useful gift of nature. It is the most abundant and essential natural resource. It covers nearly 70% of the earth's surface. It is estimated that the hydrosphere contains about 1360 million cubic kilometer ($1.3 \times 10^{18} \text{ m}^3$) of water. Of this, about 97% is in the oceans and inland seas, which is not suitable for human consumption because of its high salt content. Of the remaining 3%, 2% is locked in the glaciers and polar ice caps and only 1% is available as fresh water in rivers, lakes, streams, reservoirs and ground water, which is suitable for human consumption.

Water on Earth



Source www.aid-n.com/earths-water-resources-in-the-world/earths-water-resources-water-on-earth published Nov 8, 2012.

2.2 Sources of Water

The chief sources of water are

1. Surface water
2. Ground water
3. Rain water

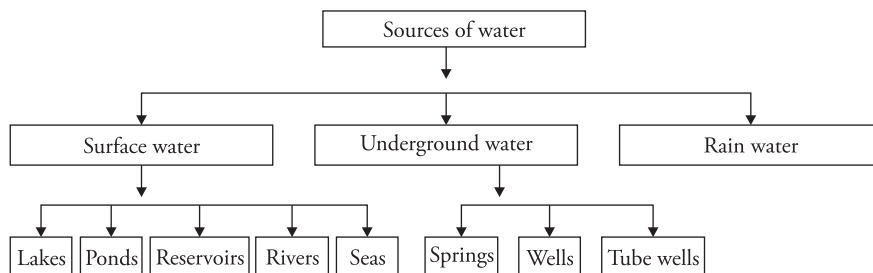
- (1) **Surface water sources** These include lakes, ponds, reservoirs, streams, rivers, seas and oceans.

River water It contains dissolved minerals of the soils such as chlorides, sulphates and bicarbonates of sodium, calcium, magnesium and iron. It also contains organic matter derived from dead and decayed plants and animals; besides this, it contains sand and soil in suspension.

Water of lakes, ponds and reservoirs They contain less of dissolved minerals but are rich in organic matter.

Sea water It is the most impure form of natural water. It contains on an average 3.5% of dissolved salts, of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

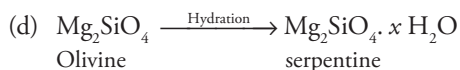
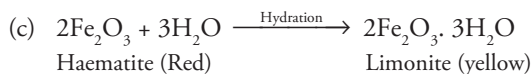
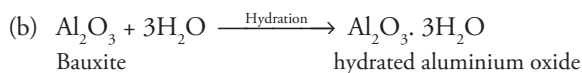
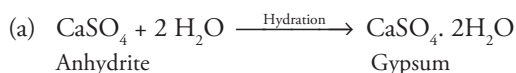
- (2) **Underground water sources** This is the water accumulated under the ground through seepage. It is obtained from wells, tube wells, springs, etc. Underground water is relatively free from suspended impurities because it is filtered as the water moves down through different layers of soil. The filtration also removes biological contamination. However, underground water is rich in dissolved salts.
- (3) **Rain water** It is considered to be the purest form of water. However, it dissolves large amount of gases and suspended solid particles from the atmosphere. Rain water is divided between the two sources, a part of it seeps down to underground water tables and a part of it goes to the surface sources like rivers, ponds, lakes and reservoirs.



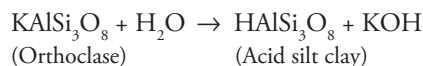
2.3 Effect of Water on Rocks and Minerals

Water brings about the weathering of rocks by various chemical processes like

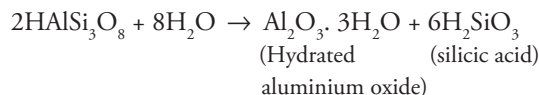
- (i) **Dissolution** Certain minerals and salts dissolve in water creating holes in the rock. This leads to the weakening of the rock that may ultimately lead to its collapse. Minerals like halite dissolve directly in water.
- (ii) **Hydration** Under humid conditions and in the presence of moisture, the soil-forming minerals in the rocks swell leading to the increase in their volume. This further leads to the disintegration of the rocks in which these minerals are present. Some common examples are as follows:



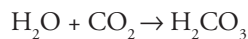
- (iii) **Hydrolysis** Water dissociates into H^+ and OH^- ions that combine with minerals to form new compounds. The silicates combine with water, forming clays.



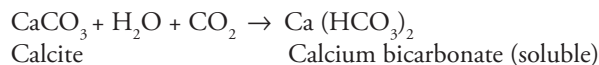
The acid silt clay further recombines as



- (vi) **Carbonation** Atmospheric carbondioxide dissolves in water to form carbonic acid.

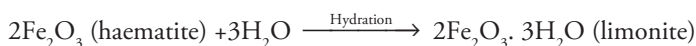
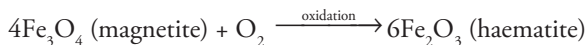


This carbonic acid reacts with the rocks and minerals and dissolves them.



The removal of CaCO_3 that holds the sand particles together leads to disintegration of rocks.

- (v) **Oxidation** The oxygen present in soil water and atmosphere leads to oxidation and hydration



The affected rock becomes reddish brown because of oxidation. The rock weakens and crumbles easily.

2.4 Common Impurities of Water

Water is a very good solvent; therefore, it dissolves a large number of substances in it. The common impurities present in water are as follows

A. *Dissolved impurities*

- These may be dissolved salts like carbonates, bicarbonates, nitrates, sulphates and chlorides of calcium, magnesium, sodium, potassium, iron, manganese, aluminium, etc.
- Dissolved gases like O_2 , CO_2 , SO_2 , NH_3 , N_2 and oxides of nitrogen also fall in this category.

- B. **Colloidal impurities** These are those impurities whose particle size varies from 1 to 100 nm. It consists of finely divided silica, clay, aluminium hydroxide, ferric hydroxide, organic waste products, coloring matter, etc.

- C. **Suspended impurities** These are impurities with particle size greater than 100 nm and can be removed by filtration or settling. They may be organic, inorganic or microorganism.

- **Organic impurities** consist of animal and vegetable matter, wood pieces, leaves, oil globules, etc.
- **Inorganic impurities** include clay, silica, sand, etc.
- **Microorganisms** include various types of algae, protozoa, bacteria and fungi.

Suspended impurities give turbidity and color to water. Microorganisms are the main cause of water-borne diseases.

Characteristics imparted by impurities in water

Water is a very good solvent and dissolves various impurities in it. These substances present in water affect the characteristics of water in various ways. They alter the physical, chemical and biological characteristics of water. Let us discuss them one by one.

Physical characteristics

- Presence of salts like iron, manganese, industrial effluents, dyes from industries and other salts impart color to water.
- Presence of sand and silt make the water turbid.
- Salts also alter the taste of water. Presence of salts of sodium and potassium makes the water salty. Aluminium, manganese and iron make the water bitter. Presence of sodium bicarbonate gives soapy taste to water.
- Organic matter, decaying vegetation, algae, fungi and sewage impart a characteristic foul odor to water.

Chemical characteristics

Wastes, including organic and inorganic chemicals like dyes, molasses, fertilisers, acids, alkalies from industries insecticides, pesticides, liquors, wastes from tanneries and gases like NH_3 and H_2S produced by anaerobic decomposition, alter the pH, alkalinity, acidity, hardness and chemical characteristics of water and make it unfit for domestic and industrial use.

Biological characteristics

The biological impurities like algae, fungi, pathogens and other microorganisms present in water either naturally or due to discharge of organic waste from domestic sewage, industrial houses or produced by the natural decay of organic matter all adversely affect the biological characteristics of water and make it unfit for domestic use, adversely affecting human health, aquatic flora and fauna.

Table 2.1 Common impurities in water and their effects

Type	Constituents	Effect
1. Suspended impurities	(a) Bacteria	Some causes diseases
	(b) Algae, protozoa	Odor, color, turbidity, diseases
	(c) Silts	Turbidity
2. Dissolved Impurities	(d) Salts	Alkalinity
	(i) Ca and Mg – bicarbonate	Alkalinity, hardness
	– Carbonates	Hardness
	– Sulphate	Hardness
	– Chloride	Hardness
	(ii) Na–bicarbonate	Alkalinity
	– Carbonate	Alkalinity
	– Sulphate	Foaming
	– Fluoride	Dental problems
	– Chloride	Affects taste
	(b) Metals and compounds	
	(i) Oxide of iron	Taste, color, corrosion, hardness
	(ii) Mn	Black and brown color
	(iii) Pb	Poisoning
	(iv) As	Poisoning
	(v) Ba	Effect on heart and nerves

(vi) Cd	Illness
(vii) CN	Fatal
(viii) B	Nervous system
(ix) Se	Highly toxic
(x) Ag	Discoloration of skin, eyes
(xi) Nitrates	Poisoning, color, blue baby syndrome
(c) Vegetable dyes	Acidity
(d) Gases—Oxygen	Corrodes metals
—Hydrogen sulphide	Odor, acidity, corrosiveness
—Carbon dioxide	acidity, corrosion

2.5 Water Quality Standards

Importance of water quality standards

Water is widely used both in domestic and industrial life. Natural water, no matter how pure, contains some or the other impurities. Water quality standards are important because they help to identify the water quality, problems caused by improper treatment of waste water discharge, run off, addition of fertilisers, chemicals from agricultural areas and so on. The parameters for water quality are decided according to its use. Work in the area of water quality tends to be focused on whether water is treated for human consumption or environmental purpose. It is important to specify water quality standards for the purpose of safety of human beings, drinking characteristics and for the health of ecosystems.

Environmental water quality also called ambient water quality specifies the quality of water in water bodies like lakes, rivers and oceans. Ambient water quality standards vary significantly because of different environmental conditions, ecosystem and intended human uses.

The water quality parameters or characteristics for which analysis is carried out generally fall into three groups:

1. Physical characteristics
2. Chemical characteristics
3. Biological characteristics

(1) Physical characteristics

These are characteristics that respond to touch, taste, sight, etc. These include turbidity, temperature, odor, color and taste.

- (a) **Color** Clean water should be colorless. The presence of color in water indicates the presence of various minerals, decomposed organic matter like leaves, roots, organic and inorganic wastes, wastes from textile mill, paper pulp industries, food-processing industries, domestic wastes, wastes from laundry, dyeing, dairy products, etc.
- (b) **Taste and odor** Water should be odorless and should have a fairly good taste. There are no specific units to measure these parameters, but generally decaying organic matter imparts odor and bad taste to water. The minimum odor that can be detected is called threshold odor number (TON). The value of TON is determined as follows:

$$\text{TON} = \frac{A+B}{A}$$

A = Volume of sample in mL; B = Volume of distilled water (i.e., odor-free water in mL).

- (c) **Temperature** It is an important water quality parameter. High temperature indicates thermal pollution and disturbs aquatic ecosystem by reducing the dissolved oxygen in water.
- (d) **Electrical conductivity** It gives an idea about the dissolved solids in water. Greater the amount of dissolved solids, higher will be the conductivity. It can be measured easily with the help of conductivity meter. The average value of conductivity for potable water should be less than 2 $\mu\text{mho/cm}$ ($\mu\text{S/cm}$).

(2) Chemical characteristics

Some important chemical characteristics are pH, hardness, alkalinity, total dissolved solids, chlorides, fluorides, sulphates, phosphates, nitrates, metal, etc.

- (a) **pH** The pH of normal drinking water is 6.5–8.5. It can be measured with the help of pH meter using a combined electrode (a glass electrode and a calomel electrode as reference electrode). pH scale ranges from 0 to 14. pH 7 indicates neutral solution, less than 7 is acidic, whereas greater than 7 signifies alkaline or basic water.
- (b) **Hardness** It expresses the concentration of calcium and magnesium ions in water in terms of equivalent of CaCO_3 . The maximum acceptance limit is 500 ppm.
- (c) **Total dissolved solids (TDS)** The maximum permissible limit is 500 mg/L. TDS includes both organic and inorganic dissolved impurities. It can be measured by evaporating a sample to dryness and then weighing the residue.
- (d) **Total solids** This includes both the dissolved solids as well as suspended impurities.
- (e) **Dissolved oxygen** It is an important water quality parameter. Higher the amount of DO better is the quality of water. Normal water contains 4.7 mg/L of DO. Lesser amount of DO in water indicates pollution in water. Winkler or iodometric methods using membrane electrode is used for measuring DO in water.
- (f) **Chlorides** Its amount in water should be less than 250 ppm. High percentage of chloride in water harms metallic pipes as well as agriculture crops.
- (g) **Fluorides** Maximum permissible limit is 1.5 ppm. The amount of fluoride in water sample can be determined using an ion meter. Excess of fluoride causes discoloration of teeth, bone fluorosis and skeletal abnormalities.
- (h) **Sulphates** Permissible limit is 250 ppm. These are generally found associated with calcium, magnesium and sodium ions. It leads to scale formation in boilers, causes boiler corrosion and imparts odor to water.
- (i) **Nitrates** Its concentration in drinking water should not exceed 45 mg/L. Excessive nitrates in drinking water causes 'methemoglobinemia' or blue baby syndrome in infants. Nitrates dissolve in water because of leaching of fertilisers from soil and nitrification of organic matter.

(3) Biological characteristics

Water should be free from all types of bacteria, viruses, protozoa and algae. The coliform count in any sample of 100 mL should be zero.

(4) Bacteriological standards

(i) **Water entering the distribution system** Coliform count in any sample of 100 mL should be zero. A sample of water entering the distribution system that does not confirm to this standard calls for an immediate investigation into both the efficacy of the purification process and the method of sampling.

(ii) **Water in the distribution system** It shall satisfy these three criteria:

(a) *E. coli* count in 100 mL of any sample should be zero.

(b) Coliform organism should not be more than 10 per 100 mL of any sample.

(c) Coliform organism should not be present in 100 mL of any two consecutive samples or more than 5% of the samples collected for the year.

(5) **Virological standards** 0.5 mg/L of free residual chlorine for 1 h is sufficient to inactivate virus, even in water that was originally polluted. This free residual chlorine should be present in all disinfected supplies in area suspected of infectious hepatitis to inactivate virus and also bacteria. For water supply in such areas, 0.2 mg/L of free residual chlorine for half an hour should be insisted.

The Indian standard for drinking water prescribed by the Bureau of Indian Standards and Indian Council of Medical Research are shown in Table 2.2.

Table 2.2 BIS 105000: Indian standard of drinking water specification

S.No	Substance or characteristic	Acceptable limit	Cause of rejection
	Essential characteristics		
1	Color (units on platinum – cobalt scale)	5	25
2	Odor	Unobjectionable	Unobjectionable
3	Taste	Agreeable	Agreeable
4	Turbidity (JTU, Max)	5	10
5	pH value	7.0–8.5	6.5–9.2
6	Total hardness (as CaCO ₃) mg/L	200	600
7	Iron (as Fe in mg/L)	0.1	1.0
8	Chlorides (as Cl in mg/L)	200	1000
9	Residual, free chloride, mg/L	0.2	-
	Desirable characteristics		
10	Total dissolved solids mg/L	500	1500
11	Calcium (as Ca), mg/L	75	200
12	Copper (as Cu), mg/L	0.05	1.5
13	Manganese (as Mn), mg/L	0.05	0.5
14	Sulphate (as SO ₄), mg/L	200	400
15	Nitrate (as NO ₃), mg/L	45	45

16	Fluoride (as F), mg/L	1.0	1.5
17	Phenolic compounds (as C ₆ H ₅ OH), mg/L	0.001	0.002
18	Mercury (as Hg), in mg/L	0.001	No relaxation
19	Cadmium (as Cd), in mg/L	0.01	No relaxation
20	Selenium (as Se), in mg/L	0.01	No relaxation
21	Arsenic (as As), in mg/L	0.05	No relaxation
22	Cyanide (as CN), in mg/L	0.05	No relaxation
23	Lead (as Pb), in mg/L	0.1	No relaxation
24	Zinc (as Zn), in mg/L	5	15
25	Anionic detergents (as MBAS), in mg/L	0.2	1.0
26	Chromium (as Cr ⁶⁺), mg/L	0.05	No relaxation
27	Polynuclear aromatic hydrocarbons (as PAH), mg/L	0.2	0.2
28	Mineral oil, mg/L	0.01	0.3
29	Pesticides, mg/L	Absent	0.001
30	Radioactive materials (i) Gross alpha emitters pCi/L (ii) Gross beta emitters pCi/L	3 30	3 30
31	Alkalinity, mg/L	200	600
32	Aluminium (as Al), mg/L	0.03	0.2
33	Boron, mg/L	1	1

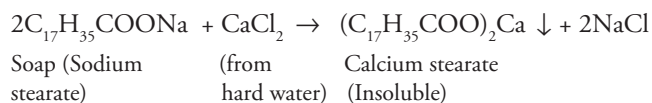
Note: The values indicated under the column 'acceptable' are the limits upto which water is generally acceptable to consumers. Values in excess of those mentioned under 'acceptable' render the water not acceptable but still may be tolerated in the absence of alternative and better source upto the limits indicated under column 'cause of rejection' above which the supply will have to be rejected.

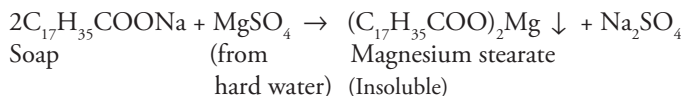
2.6 Hardness of Water

Definition It is defined as the characteristic of water that prevents lathering of soap. Originally, it was defined as the soap-consuming capacity of water.

Causes Hardness is due to the presence of certain soluble salts of calcium and magnesium in water. A sample of hard water, when treated with soap (sodium or potassium salts of higher fatty acids like oleic, palmitic or stearic acid), does not form lather or foam but forms a white precipitate or scum instead. This is because of the formation of insoluble salts of calcium and magnesium.

Chemical reactions involved are





Other salts of calcium and magnesium like CaSO_4 , $\text{Ca}(\text{NO}_3)_2$ and MgCl_2 also react in a similar way forming insoluble precipitates of calcium and magnesium salts of higher fatty acids.

Table 2.3 Difference between hard and soft water

S.No	Hard water	Soft water
1	Water that does not form lather with soap but forms white precipitate	Water that produces lather or foam easily with soap is called 'soft water'
2	It contains soluble salts of calcium magnesium and other heavy metal ions like Al^{3+} , Fe^{3+} , and Mn^{2+} dissolved in it	It does not contain dissolved salts of calcium and magnesium
3	In hard water, the cleaning properties of soap is depressed and lot of soap is wasted in bathing and washing	The cleaning quality of soap is not depressed hence it is good for washing and cleaning
4	Owing to dissolved hardness, boiling point of water is elevated, therefore more fuel and time is required for cooking	Less fuel and time is required for cooking

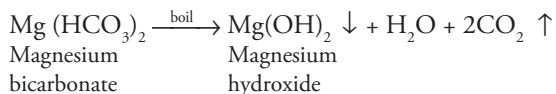
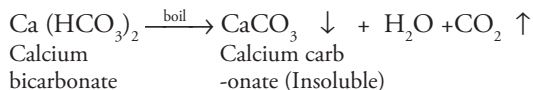
Types of hardness

Hardness is of two types:

1. Temporary hardness
2. Permanent hardness

(1) Temporary hardness

- (a) It is also called carbonate hardness or alkaline hardness. It is called alkaline hardness because it is due to the presence of bicarbonate, carbonate and hydroxide and can be determined by titration with HCl using methyl orange as an indicator.
- (b) It can be removed by boiling of water. During boiling, the bicarbonates are decomposed forming insoluble carbonates or hydroxides that are deposited at the bottom of the vessel.



(2) Permanent hardness

- (a) It is also called non-carbonate or non-alkaline hardness.

- (b) It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals.
- (c) Salts mainly responsible for permanent hardness are
 CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, etc.
- (d) It cannot be removed by simple boiling but can be removed by special chemical methods like lime–soda process, zeolite method, etc.

Table 2.4 Comparison between temporary and permanent hardness

S.No	Temporary hardness	Permanent hardness
1	Also called carbonate hardness or alkaline hardness	Also called non-carbonate or non-alkaline hardness
2	It is due to the presence of bicarbonates, carbonates of calcium and magnesium	It is due to the presence of dissolved chlorides, sulphates and nitrates of calcium, magnesium, iron and other heavy metals
3	It can be removed by boiling $\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\text{boil}} \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ $\text{Mg}(\text{HCO}_3)_2 \xrightarrow{\text{boil}} \text{Mg}(\text{OH})_2 \downarrow + \text{H}_2\text{O} + 2\text{CO}_2 \uparrow$	Cannot be removed by simple boiling but can be removed by specific chemical methods, like lime–soda process, zeolite method, etc.

Degree of hardness

Hardness is always calculated in terms of equivalent of CaCO_3 , although hardness is never present in the form of CaCO_3 . There are two basic reasons for choosing CaCO_3 as standard:

- Calculations become easy as its molecular weight is exactly 100 (and equivalent weight is exactly 50).
- It is the most insoluble salt that can be precipitated in water treatment.

Calculation of equivalents of CaCO_3

To find out hardness in a given water sample, it is essential to convert hardness due to different salts (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, CaSO_4 , MgCl_2 , MgSO_4 , etc.) in terms of equivalent of CaCO_3 . This can be done by the formula:

$$\text{Equivalent of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

- Chemical equivalent of CaCO_3 is 50
- Chemical equivalent of salt = $\frac{\text{Molecular weight}}{\text{Valency}}$
- Chemical equivalent of acid = $\frac{\text{Molecular weight}}{\text{Basicity}}$

Basicity is the number of replaceable hydrogen ions in an acid.

- Chemical equivalent of base = $\frac{\text{Molecular weight}}{\text{Acidity}}$

Acidity is the number of replaceable hydroxyl ions in a base.

The ratio = $\frac{\text{Chemical equivalent of CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$, is constant for a particular compound and is called multiplication factor.

Hence, equivalent of CaCO_3 = mass of hardness producing substance \times multiplication factor.

The formula and multiplication factor for different salts are tabulated in Table 2.5.

Table 2.5 Formula and multiplication factor for different salts

Dissolved salt/ ion	Molar mass	Chemical equivalent	Multiplication factor = $\frac{\text{Eq Wt of CaCO}_3}{\text{Eq Wt of hardness producing substance}}$
$\text{Ca}(\text{HCO}_3)_2$	162	$162/2 = 81$	$\frac{100/2}{162/2} = \frac{100}{162}$
$\text{Mg}(\text{HCO}_3)_2$	146	$146/2 = 73$	$\frac{100/2}{146/2} = \frac{100}{146}$
CaSO_4	136	$136/2 = 68$	$\frac{100/2}{136/2} = \frac{100}{136}$
CaCl_2	111	$111/2 = 55.5$	$\frac{100/2}{111/2} = \frac{100}{111}$
MgSO_4	120	$120/2 = 60$	$\frac{100/2}{120/2} = \frac{100}{120}$
MgCl_2	95	$95/2 = 47.5$	$\frac{100/2}{95/2} = \frac{100}{95}$
CaCO_3	100	$100/2 = 50$	$\frac{100/2}{100/2} = \frac{100}{100}$
MgCO_3	84	$84/2 = 42$	$\frac{100/2}{84/2} = \frac{100}{84}$
$\text{Mg}(\text{NO}_3)_2$	148	$148/2 = 74$	$\frac{100/2}{148/2} = \frac{100}{148}$
Ca^{++}	40	$40/2 = 20$	$\frac{100/2}{40/2} = \frac{100}{40}$
Mg^{++}	24	$24/2 = 12$	$\frac{100/2}{24/2} = \frac{100}{24}$

HCO_3^-	61	$61/1 = 61$	$\frac{100/2}{61/1} = \frac{100}{2 \times 61} = \frac{100}{122}$
CO_3^{2-}	60	$60/2 = 30$	$\frac{100/2}{60/2} = \frac{100}{60}$
OH^-	17	$17/1 = 17$	$\frac{100/2}{17/1} = \frac{100}{2 \times 17} = \frac{100}{34}$
H^+	1	1	$\frac{100/2}{1/1} = \frac{100}{2}$
CO_2	44	$44/2 = 22$	$\frac{100/2}{44/2} = \frac{100}{44}$
HCl	36.5	$36.5/1 = 36.5$	$\frac{100/2}{1 \times 36.5} = \frac{100}{2 \times 36.5} = \frac{100}{73}$
H_2SO_4	98	$98/2 = 49$	$\frac{100/2}{98/2} = \frac{100}{98}$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	$278/2 = 139$	$\frac{100/2}{278/2} = \frac{100}{278}$
$\text{Al}_2(\text{SO}_4)_3$	342	$342/6 = 57$	$\frac{100/2}{342/6} = \frac{100 \times 3}{342} = \frac{50}{57}$
NaAlO_2	82	$82/1 = 82$	$\frac{100/2}{82/1} = \frac{100}{82 \times 2} = \frac{100}{164}$

Solved Examples

1. A water sample contains 248 mg CaSO_4 per liter. Calculate the hardness in terms of CaCO_3 equivalent.

Solution

Weight of CaSO_4 per liter = 248 mg

Hardness in terms of CaCO_3 equivalent = ?

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

$$\frac{248 \times 100/2}{136/2} = 182.35 \text{ ppm.}$$

2. How many grams of FeSO_4 dissolved per liter gives 300 ppm of hardness?

(Fe = 56, S = 32, O = 16, Ca = 40, C = 12)

Solution

1 mole of FeSO_4 causes hardness equivalent to that caused by 1 mole of CaCO_3 because 1 mole of any two substances contain equal number of molecules, that is, Avogadro's number of molecules.

\therefore 1 mole $\text{FeSO}_4 = 1$ mole of CaCO_3

or, $56 + 32 + 64 = 152$ g of $\text{FeSO}_4 = 40 + 12 + 48 = 100$ g of CaCO_3

\therefore 100 ppm of CaCO_3 equivalent hardness is caused by 152 ppm of FeSO_4 or,

300 ppm of hardness will be caused by $\frac{152}{100} \times 300 = 456$ ppm of $\text{FeSO}_4 = 456 \text{ mg/L} = 0.456 \text{ g/L}$ of FeSO_4

[Ans = 0.456 g/L]

Alternative method

Calculation by direct application of formula

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of hardness producing substance}}$$

Let mass of hardness producing substance, that is, $\text{FeSO}_4 = x$ mg

$$\text{Then } 300 = \frac{x \times 100 / 2}{152 / 2}$$

$$\text{or } 300 = \frac{x \times 100}{152} = 456 \text{ ppm} = 456 \text{ mg/L} = 0.456 \text{ g/L}$$

Units of hardness and their interrelationship

- (i) **Parts per million (ppm)** It is defined as the number of parts by weight of CaCO_3 equivalent hardness present in million (10^6) parts by weight of water.

1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

- (ii) **Milligrams per liter (mg/L)** It is defined as the number of milligrams of CaCO_3 equivalent hardness present per liter of water.

1mg/L = 1mg of CaCO_3 equivalent hardness in one liter of water

Since weight of 1 liter of water = 1 kg

$$= 1000 \text{ g} = 1000 \times 1000 = 10^6 \text{ mg}$$

1mg/L = 1mg of CaCO_3 per 10^6 mg of water.

= 1 part of CaCO_3 per 10^6 parts of water.

= 1 ppm.

Thus mathematically, 1ppm = 1mg/L.

- (iii) **Degree Clarke ($^\circ\text{Cl}$)** It is defined as the number of grains (1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water.

1 $^\circ$ Clarke = 1 grain of CaCO_3 equivalent hardness per gallon of water

\therefore 1 grain = 1/7000 lb (pounds)

And 1 gallon = 10 lb

1 grain/gallon = 1/7000 lb/10 lb

$$= 1:70,000$$

1 $^\circ$ Cl can also be defined as the number of parts of CaCO_3 equivalent hardness per 70,000 parts of water.

- (iv) **Degree French ($^\circ\text{Fr}$)** It is defined as the number of parts of CaCO_3 equivalent hardness per 10^5 parts of water. Thus,

1 $^\circ$ Fr = 1 part of CaCO_3 equivalent hardness per 10^5 parts of water.

Relationship between different units of hardness As,

1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

1mg/L = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

1 $^\circ$ Cl = 1 part of CaCO_3 equivalent hardness in 70000 parts of water.

1 $^\circ$ Fr = 1 part of CaCO_3 equivalent hardness in 10^5 parts of water.

Hence,

$$10^6 \text{ ppm} = 10^6 \text{ mg/L} = 70,000 \text{ }^\circ\text{Cl} = 10^5 \text{ }^\circ\text{Fr}$$

Dividing by 10^6

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07 \text{ }^\circ\text{Cl} = 0.1 \text{ }^\circ\text{Fr}$$

Similarly,

$$1 \text{ }^\circ\text{Cl} = 1.433 \text{ }^\circ\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L}$$

$$1 \text{ }^\circ\text{Fr} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7 \text{ }^\circ\text{Cl}$$

Solved Examples

- Three samples P, Q and R were analysed for their salt contents.
 - Sample P was found to contain 155 mg of magnesium carbonate per liter.
 - Sample Q was found to contain 800 mg of calcium nitrate and 2.5 mg of silica and 5.1 mg of sodium chloride per liter.
 - Sample R was found to contain 15 g of potassium nitrate and 3 g of calcium carbonate per liter. Find the hardness of all the above three samples in ppm and in grains per gallon.

Solution

Sample	Constituent	Amount mg/L	Equivalents of CaCO_3
P	MgCO_3	155 mg/L	$\frac{155 \times 100 / 2}{84 / 2} = 184.52 \text{ mg/L}$
Q	$\text{Ca(NO}_3)_2$	800 mg/L	$\frac{800 \times 100 / 2}{164 / 2} = 487.80 \text{ mg/L}$
R	CaCO_3	3 g/L or 3000 mg/L	$\frac{3000 \times 100 / 2}{100 / 2} = 3000 \text{ mg/L}$

∴ Hardness of the three samples in ppm

Sample P = 184.52 ppm; Sample Q = 487.80 ppm; Sample R = 3000 ppm.

Hardness of the three samples in grains/gallon or degree Clarke

Since 1 ppm = 0.07 °Cl = 0.07 grains/gallon

Sample P = 184.52 ppm × 0.07 = 12.91 grains/gallon

Sample Q = 487.80 ppm × 0.07 = 34.146 grains/gallon

Sample R = 3000 ppm × 0.07 = 210 grains/gallon.

2. A sample of water on analysis was found to contain $\text{Ca(HCO}_3)_2 = 4 \text{ mg/L}$; $\text{Mg(HCO}_3)_2 = 6 \text{ mg/L}$; $\text{CaSO}_4 = 8 \text{ mg/L}$; $\text{MgSO}_4 = 10 \text{ mg/L}$. Calculate the temporary, permanent and total hardness of water in ppm, °Fr and °Cl [Mol wt of $\text{Ca(HCO}_3)_2 = 162$, $\text{Mg(HCO}_3)_2 = 146$; $\text{CaSO}_4 = 136$; $\text{MgSO}_4 = 120$].

Solution

Conversion into CaCO_3 equivalent

Constituent	Amount	Equivalent of CaCO_3
$\text{Ca(HCO}_3)_2$	4 mg/L	$\frac{4 \times 100 / 2}{162 / 2} = 2.469 \text{ mg/L}$
$\text{Mg(HCO}_3)_2$	6 mg/L	$\frac{6 \times 100 / 2}{146 / 2} = 4.110 \text{ mg/L}$
CaSO_4	8 mg/L	$\frac{8 \times 100 / 2}{136 / 2} = 5.882 \text{ mg/L}$
MgSO_4	10 mg/L	$\frac{10 \times 100 / 2}{120 / 2} = 8.333 \text{ mg/L}$

Temporary hardness is due to $\text{Ca(HCO}_3)_2$ and $\text{Mg(HCO}_3)_2$.

Hence, temporary hardness = 2.469 + 4.110
= 6.579 mg/L or 6.579 ppm

Since $1\text{ mg/L} = 1\text{ ppm} = 0.07^\circ\text{Cl} = 0.1^\circ\text{Fr}$

$$= 6.579 \times 0.1^\circ\text{Fr} = 0.6579^\circ\text{Fr}$$

$$= 6.579 \times 0.07^\circ\text{Cl} = 0.4605^\circ\text{Cl}$$

Permanent hardness is due to salts of CaSO_4 and MgSO_4 , Hence

$$\text{Permanent hardness} = 5.882 + 8.333 = 14.215 \text{ mg/L} = 14.215 \text{ ppm}$$

$$= 14.215 \times 0.1 = 1.42150^\circ\text{Fr}$$

$$= 14.215 \times 0.07 = 0.995^\circ\text{Cl}$$

Total hardness = Temporary hardness + Permanent hardness

$$= 6.579 + 14.215 = 20.794 \text{ mg/L} = 20.794 \text{ ppm}$$

$$= 20.794 \times 0.1 = 2.0794^\circ\text{Fr}$$

$$= 20.794 \times 0.07 = 1.4555^\circ\text{Cl}$$

Practice Problems

1. A water sample contains $\text{Ca}(\text{HCO}_3)_2 = 32.4 \text{ mg/L}$, $\text{Mg}(\text{HCO}_3)_2 = 29.2 \text{ mg/L}$, $\text{CaSO}_4 = 13.5 \text{ mg/L}$. Calculate the temporary and permanent hardness of water.

[Ans Temporary hardness = $20 + 20 = 40 \text{ ppm}$; permanent hardness = 9.926 ppm]

2. A sample of water on analysis gives the following data:

$$\text{Ca}(\text{HCO}_3)_2 = 24.1^\circ\text{French}; \text{CaSO}_4 = 3.2^\circ\text{French}; \text{MgCl}_2 = 9.5^\circ\text{French}$$

$$\text{SiO}_2 = 2.1^\circ\text{French}; \text{MgSO}_4 = 8.2^\circ\text{French}$$

Calculate the temporary and permanent hardness on $^\circ\text{Clarke}$ and ppm scale.

[Ans Temporary hardness = $14.88^\circ\text{French} = 10.41^\circ\text{Clarke} = 148.88 \text{ ppm}$;
permanent hardness = $19.18^\circ\text{Fr} = 13.426^\circ\text{Cl} = 191.8 \text{ ppm}$]

3. A sample of water on analysis has been found to contain the following impurities

$$\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg/L}; \text{Mg}(\text{NO}_3)_2 = 44.4 \text{ mg/L}; \text{MgSO}_4 = 36 \text{ mg/L};$$

$$\text{MgCl}_2 = 19.0 \text{ mg/L} \text{ and } \text{CaCO}_3 = 30 \text{ mg/L}.$$

Calculate the temporary and permanent hardness in ppm and $^\circ\text{Clarke}$.

[Ans Temporary hardness = 40 ppm and 2.8°Clarke ;
permanent hardness = 80 ppm and 5.6°Clarke]

2.7 Disadvantages of Hard Water

(1) In Industries

Large quantities of water is used for steam generation in industries like textile, paper, sugar, dyeing, pharmaceutical, etc.

- (a) *Steam generation in boilers* The use of hard water in boilers causes problems like scale and sludge formation, boiler corrosion, caustic embrittlement, priming and foaming, etc (discussed in detail in Section 2.9).

- (b) *Sugar industries* Salts dissolved in hard water cause problems in crystallisation of sugar.
- (c) *Paper industries* The cations (Ca^{2+} , Mg^{2+} , Fe^{2+} etc) present in hard water react with the chemicals involved in different steps of paper manufacturing. This produces various unwanted side products and undesirable effects like loss of gloss and smoothness, change in color of paper, etc.
- (d) *Textile industries* During washing of the fabric or yarn with hard water the calcium and magnesium salts stick to the surface causing undesirable changes in color or texture of fabric.
- (e) *Dyeing industries* The salts dissolved in hard water react with the functional groups present in the dyes causing precipitation or change in shade.
- (f) *Pharmaceutical industry* Use of hard water in the preparation of drugs can lead to the production of undesirable products that may be harmful or even poisonous.

(2) ***In domestic usage***

- (a) *Drinking* Taste of soft water is better than hard water. The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children. However, hard water can have bad affect on our appetite and digestive system; sometimes it produces calcium oxalate that causes different urinary problems.
- (b) *Cooking* The boiling point of hard water increases because of the presence of various salts; this causes wastage of time and fuel.
- (c) *Bathing and washing* As hard water does not form lather or foam with water, it adversely affects the cleaning properties of soap and a lot of it is wasted because of production of sticky precipitates of calcium and magnesium. The production of sticky precipitate continues till all the calcium and magnesium salts present in water are precipitated, after which the soap starts giving lather with water.

Moreover, the sticky precipitate adheres on the cloths giving stains, streaks and spots.

2.8 Water for Industries

Water is a prime requirement for any industry. In fact, industries are generally located in areas where water is abundantly available. Water is used in industries for washing, cooling, steam generation, as a heat-transfer medium, for dilution, as a solvent, for dust suppression, to reduce pollution, etc. The quality of water has a major bearing on the safety and durability of the machinery. It affects the life of the machinery and also the quality of the products formed. Each industry has its own specifications for water, depending upon the use to which the latter is kept. The specifications of water used in major industries is tabulated in Table 2.6.

Table 2.6 Specifications of water for major industrial use

S.No	Name of the industry/unit	Specifications of water to be used
1.	Boiler feed water	Should have zero hardness, it should be free from dissolved gases, acids, alkalies and organic matter. The presence of hardness causes problems like boiler corrosion, scale and sludge formation, priming, foaming and carry over. Acids and gases like CO ₂ in water lead to boiler corrosion. Alkalies in water cause caustic embrittlement.
2.	Cooling systems	Should have little dissolved solids, less amount of dissolved gases as dissolved gases cause corrosion, should be free from organic matter, should not promote the growth of slime and algae as the spray nozzles and cooling pipes may be clogged due to the deposition of solids.
3.	Food production industries like confectionary, dairies, distilleries, beverages, sugar industries, etc.	Water should be soft, should not be acidic or alkaline and should not contain dissolved gases, organic matter, pathogens and fungi. Water should confirm to the standards of drinking water. Presence of salts in water modifies the taste of the product, presence of alkalinity neutralises the acids in the fruits and modifies the taste. In sugar industries, the presence of salts causes crystallisation. Presence of pathogens spoil the food products creating bad odor.
4.	Textiles	Should be soft and free from turbidity, color-forming ions like iron, manganese and organic matter. Presence of salts leads to spots and deposit formation on the textiles. Salts can lead to unwanted product formation modifying the color of the dye in the dyeing process. Hard water precipitates basic dyes and decreases the solubility of acidic dyes. These salts produce insoluble precipitates that stain the cloth and cause uneven dyeing.
5.	Laundry	Should be free from hardness-producing substances. Should not contain iron and manganese salts because hard water consumes soap and does not clean properly. Can cause staining on the cloth due to the formation of iron soap.
6.	Paper and pulp industry	Free from hardness and alkalinity, free from silica, lime, magnesia, iron salts, turbidity-producing material and color should be absent because hardness-producing ions react with the chemicals used for processing paper. Silica may produce cracks in the paper and may decompose the resin films.
7.	Pharmaceutical industries	Water should be very pure, highly sterilised and free from all types of salts, pathogens and should confirm to the standards of potable water. Presence of salts in water can lead to the formation of undesirable products, some of which may be poisonous. Presence of pathogens can lead to infection in the patient.

2.9 Boiler Problems with Hard Water

Boiler feed water should correspond with the following composition

- (i) Its hardness should be below 0.2 ppm
- (ii) Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm
- (iii) Its soda alkalinity (due to Na_2CO_3) should be 0.45–1 ppm

Excess of impurities, if present, in boiler feed water generally cause the following problems

- (i) Scale and sludge formation
- (ii) Boiler corrosion
- (iii) Caustic embrittlement
- (iv) Priming and foaming

Scale and sludge formation

Water evaporates continuously inside the boiler and the concentration of dissolved salts increases gradually. When the solution is saturated with respect to the salt concentration, the salts start precipitating out on the inner walls of the boiler. If the precipitate formed is soft, slimy and loose, it is called *sludge* and if the precipitate formed is hard and adhering on the inner walls of the boiler it is termed as *scale*.

SLUDGE

Definition It is soft, slimy and loose precipitate formed on the inner walls of the boiler.

Formation

- (a) Sludges are formed by substances which have greater solubility in hot water than in cold water like MgSO_4 , MgCl_2 , MgCO_3 , CaCl_2 etc.
- (b) They are formed at colder parts of the boiler and get collected at places where the flow rate is slow or at bends, plug opening, glass gauge connection, thereby causing even choking of the pipes.
- (c) They are poor conductors of heat.
- (d) They can be removed easily by scraping off with wire brush.

Prevention

- (i) By using softened water.
- (ii) By frequently 'blow-down operation', that is, drawing off a portion of the concentrated water from the boiler and replacing it with fresh water.

Disadvantages of sludge formation

- (i) Being poor conductors of heat they tend to waste a portion of heat generated and thus decreases the efficiency of the boiler.
- (ii) Excessive sludge formation disturbs working of the boiler.

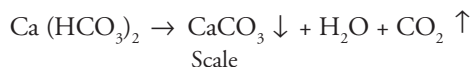
- (iii) When formed along with scale, they get entrapped in scale and both get deposited as scales.
- (iv) It settles in regions of poor water circulation such as pipe connection, plug opening, and glass gauge connection thereby choking the pipes.

SCALE

Definition They are deposits firmly sticking to the inner surface of the boiler which cannot be removed mechanically even with the help of hammer and chisel.

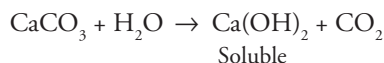
Formation of scale Scales are formed mainly due to four reasons:

(i) **Decomposition of calcium bicarbonate**

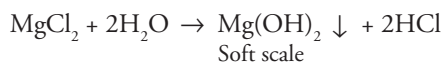


CaCO_3 scale is soft and it is the main cause of scale formation in low- pressure boilers

However in higher pressure boilers CaCO_3 is soluble due to the formation of Ca(OH)_2



- (ii) **Deposition of CaSO_4** The solubility of CaSO_4 decreases as temperature increases. CaSO_4 is soluble in cold water and is completely insoluble in superheated water. Therefore, CaSO_4 gets precipitated as hard scale on the hot portion of the boiler.
- (iii) **Hydrolysis of magnesium salts** At high temperature, dissolved magnesium salts undergo hydrolysis forming a soft scale of magnesium hydroxide.



(iv) **Formation of calcium and magnesium silicates**

Very small quantities of SiO_2 present in hard water react with calcium and magnesium forming calcium silicate (CaSiO_3) and/or magnesium silicate (MgSiO_3). These are hard scales and are extremely difficult to remove.

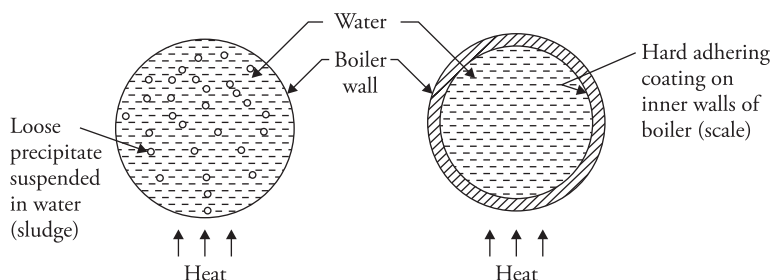


Figure 2.1 Sludge and scales in boilers

Table 2.7 Difference between scale and sludge

S.No	Sludge	Scale
1	Sludges are soft, loose and slimy precipitates	Scale are hard deposits
2	Formed at comparatively colder portions of the boiler	Formed generally at heated portion of the boiler
3	Formed by carbonate, bicarbonates of calcium and magnesium along with $Mg(OH)_2$	Formed by substances like $CaSO_4$ and silicates of calcium and magnesium
4	They are non-adherent deposits and can be easily removed	They stick very firmly to the inner surface of the boiler and are very difficult to remove
5	Decrease efficiency of boiler but are less dangerous	Decreases the efficiency of boiler and can even lead to boiler explosion
6	Can be removed by blow-down operation	Cannot be removed by blow-down operation

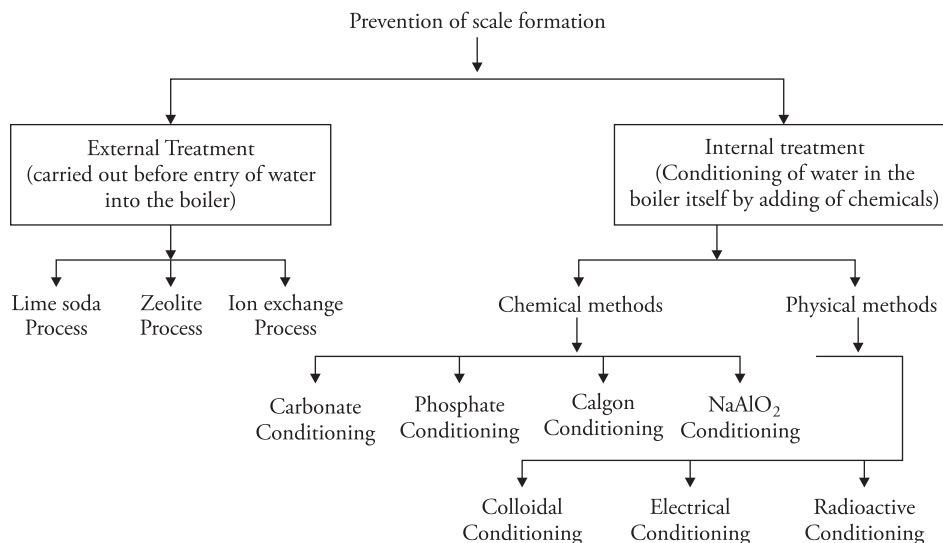
Disadvantages of scale formation

1. **Wastage of fuel** Scales have poor thermal conductivity, therefore the rate of heat transfer from boiler to the water inside is greatly reduced. Hence extra heat is to be supplied to the boiler and this increases the fuel consumption.
Wastage of fuel depends upon the thickness of the scale. Greater the thickness of the scale larger is the wastage of fuel.
2. **Lowering boiler safety** Due to scale formation which is poor conductor of heat, the boiler is to be over heated to provide steady supply of heat. Overheating makes the boiler material softer and weaker. Therefore distortion of boiler tubes takes place and the boiler becomes unsafe to bear the pressure of the steam (in high-pressure boilers).
3. **Decrease in efficiency** Deposition of scale in the valves and condensers of the boiler, chokes them partially. This results in decrease in efficiency.
4. **Danger of explosion** Due to uneven expansion the thick scales crack, as a result water comes in contact with the overheated inner walls of the boiler resulting in excessive steam formation which can lead to boiler explosion.

Removal of scale

- (i) Loosely adhering scale can be removed either by scraper or wire brush or by blow-down operation.
- (ii) Brittle scales can be removed by thermal shocks (i.e heating the boiler and then suddenly cooling with cold water).
- (iii) Hard and adherent scales can be removed by dissolving in chemicals, for example, $CaCO_3$ scale can be dissolved by using 5–10% HCl. $CaSO_4$ scale can be removed by adding EDTA since the Ca-EDTA complex is highly soluble in water.

Prevention of scale formation



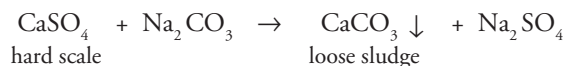
Internal Treatment

- It is also called *sequestration* or *conditioning*.
- It involves the treatment of boiler water inside the boiler by adding the suitable chemicals which either (a) precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation or (b) convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

Internal treatment methods are generally followed by blow-down operation so that accumulated sludge is removed. Important internal conditioning methods are as follows.

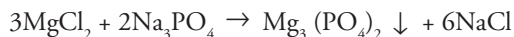
Chemical methods

1. **Carbonate conditioning** In low pressure boilers the scale formation can be avoided by adding sodium carbonate to boiler water, so that CaSO_4 is converted into calcium carbonate. Consequently deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 , which can be removed by blow-down operation.



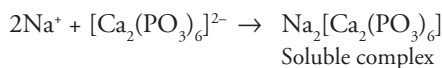
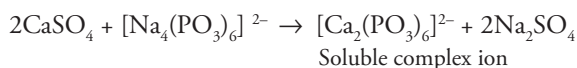
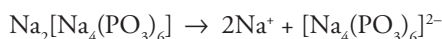
2. **Phosphate conditioning** It is used equally in low- and high-pressure boilers. Magnesium chloride which hydrolyses to form $\text{Mg}(\text{OH})_2$ scale can be removed by adding appropriate sodium phosphate NaH_2PO_4 , Na_2HPO_4 , or Na_3PO_4 .

The phosphate reacts with calcium/magnesium salts forming loose sludge of calcium or magnesium phosphate which can be removed by blow-down operation

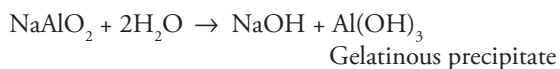


The choice of phosphate salt depends upon the alkalinity of the boiler feed water. Calcium can be precipitated properly at a pH of 9.5 or above so a phosphate is selected that adjusts pH to optimum value (9.5–10.5)

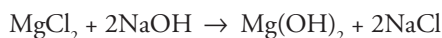
3. **Calgon conditioning** It involves adding sodium hexametaphosphate (also called calgon) to boiler water to prevent scale and sludge formation. Calgon converts the scale forming impurities into highly soluble complexes.



4. **Sodium metaaluminate (NaAlO_2) conditioning** Sodium metaaluminate gets hydrolysed forming NaOH and a gelatinous precipitate of aluminium hydroxide:



The sodium hydroxide so formed precipitates Mg^{2+} as $\text{Mg}(\text{OH})_2$



The flocculent precipitate of $\text{Mg}(\text{OH})_2$ plus $\text{Al}(\text{OH})_3$, produced inside the boiler entraps finely suspended and colloidal impurities (like oil, silica etc.). These loose precipitates are removed by blow-down process.

Physical Methods

5. **Radioactive conditioning** Tablets containing radioactive salts are placed inside the boiler at specific points. The energy radiations emitted out by these prevent the aggregation of scale forming particles.
6. **Electrical conditioning** Sealed glass bulbs, containing mercury connected to a battery are set rotating in the boiler. When water boils, mercury emits discharges which prevents scale forming particles from sticking together to form scale.

7. **Colloidal conditioning** Colloids like tannin, agar-agar gel and kerosene are added to the boiler. They form a coating around scale forming particles and thus prevent them from aggregating together to form scale. This method is effective in case of low-pressure boilers.

BOILER CORROSION

Definition It is defined as the decay or disintegration of boiler material by chemical or electrochemical attack by its environment. Boiler corrosion generally occurs due to three reasons.

1. Acid formation by dissolved salts
 2. Dissolved carbon dioxide
 3. Dissolved oxygen
- (1) **Acid formation by dissolved salts** Magnesium chloride present in the boiler feed water undergoes hydrolysis producing hydrochloric acid

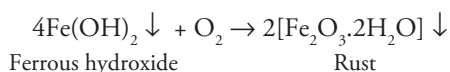


The acid thus liberated reacts with the boiler material (iron) to form ferrous hydroxide which is then converted to rust



The HCl formed in step (2) again attacks boiler material. A chain reaction is set up which causes extensive corrosion.

The $\text{Fe}(\text{OH})_2$ formed further reacts with oxygen forming rust

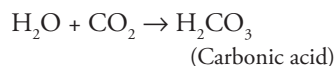


Prevention Boiler corrosion by acid formation can be prevented by adding calculated quantity of alkali which neutralises the acid thus formed.

- (2) **Dissolved carbon dioxide** The main source of CO_2 in boilers is by the decomposition of bicarbonates of calcium and magnesium.

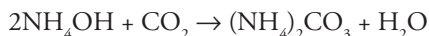


Carbon dioxide reacts with water forming carbonic acid

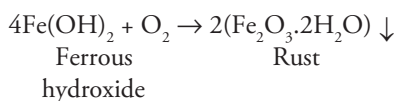
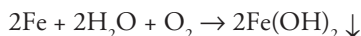


Carbonic acid has a slow corrosive effect on the boiler material.

Removal CO_2 can be removed either by adding ammonium hydroxide or by mechanical de aeration.

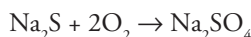
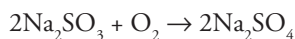
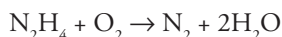


- (3) **Dissolved oxygen** Water normally contains 8 ppm of oxygen dissolved at room temperature. At high temperature, the dissolved oxygen reacts with iron of the boiler to form ferric oxide (rust):



Removal (i) By adding chemicals (ii) By mechanical de aeration

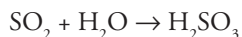
Addition of chemicals Dissolved oxygen can be removed by adding a reducing agent like hydrazine, sodium sulphite or sodium sulphide.



Aqueous hydrazine is an ideal chemical for removal of dissolved oxygen because it forms nitrogen which is harmless. Pure hydrazine cannot be used as it is explosive.

Excess of hydrazine should not be used as it decomposes to give NH_3 .

If Na_2SO_3 or Na_2S are used, Na_2SO_4 is formed, which decomposes at high temperature and produces SO_2 which reacts with water forming corrosive sulphurous acid.



- (iii) **Mechanical deaeration** The process consists of spraying water over preheated perforated plates stacked in tower. Removal of dissolved O_2 is ensured by applying high temperature and vacuum.

PRIMING AND FOAMING

PRIMING

Definition When water is heated rapidly inside the boiler or if there is a sudden increase in steam demand then water droplets are carried along the steam. This steam is termed as 'wet steam' and the formation of wet steam is called 'priming'.

Causes

1. Very high velocity of steam formation, when steam is formed at a great speed in the boiler, some droplets of water are carried along with steam.
2. Presence of considerable quantities of dissolved solids.
3. Sudden ebullition/boiling.
4. Faulty boiler design.

Minimisation of Priming

1. Controlling rapid change in steam velocities.
2. Proper boiler design (by putting anti-priming plates or dash plates).
3. Maintaining low water level.
4. Use of water without suspended impurities.
5. By blowing off scales and sludges from time to time.

FOAMING

Definition Formation of small but persistent foam or bubbles which do not break easily.

Causes The main cause of foaming is the presence of oil or alkalies in boiler feed water, which reduces the surface tension of water causing foaming.

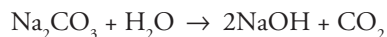
Minimisation of foaming

1. By adding anti-foaming agents like castor oil or silicic acid.
2. By adding compounds like sodium aluminates or aluminium sulphate, which removes oil from the boiler. These are hydrolysed to form $\text{Al}(\text{OH})_3$, which entraps oil drops.

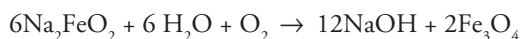
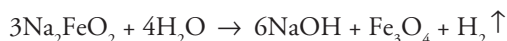
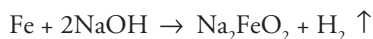
CAUSTIC EMBRITTLEMENT

It is the phenomenon in which the boiler material becomes brittle due to the accumulation of excess alkali in the boiler. Caustic embrittlement is a form of stress corrosion taking place in boilers operating at high temperature and pressure. It is caused by high alkalinity of water in the boiler, particularly at those places which are under stress such as rivets, joints and bends with the result that the metal plates become brittle.

When water is softened by lime – soda process, the excess sodium carbonate undergoes decomposition in high pressure boilers leading to the formation of NaOH.



This NaOH makes the water alkaline. The alkaline water penetrates into the minute cracks and crevices between the rivets and joints by capillary action. Inside the cracks, the water evaporates and the concentration of NaOH increases on these sites due to poor circulation of water. NaOH attacks the iron in boiler material converting it to sodium ferroate (Na_2FeO_2). A small quantity of sodium ferrite (NaFeO_2) is also formed.



It can be seen that NaOH is regenerated in the process and its concentration keeps on increasing maintaining the required environment.

The caustic embrittlement of the boiler may be explained by assuming the formation of a concentration cell as shown below:

Iron at bends, rivets, joints (stressed areas)	Concentrated NaOH solution	Dilute NaOH solution	Iron at plane surface (stress free)
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The iron in the anodic area undergoes corrosion and dissolves making the boiler material brittle.

Prevention

1. By adding tannin or lignin to the boiler water. These block the minute cracks and prevent the infiltration of NaOH.
2. Caustic embrittlement can be prevented if Na_2SO_4 is added to the boiler water, because it is useful in blocking the hair cracks. $\text{Na}_2\text{SO}_4/\text{NaOH}$ should be used in the ratio 1:1, 2:1 and 3:1 for boilers working at pressure 10, 20 and above 20 atm, respectively.
3. By using sodium phosphate instead of sodium carbonate for softening water.
4. By adjusting the pH of boiler water between 8–9.
5. Use of excess Na_2CO_3 should be avoided in the lime-soda process.

2.10 Softening Methods: External Treatment Process

External Treatment Process

Important methods employed for this process are

1. Lime-Soda Method
2. Zeolite process and
3. Ion Exchange process

The details of the above three methods are discussed as follows.

Lime soda process

It is an important softening process.

Principle The basic principle of this process is to convert all the soluble hardness causing impurities into insoluble precipitates which can be removed by sedimentation and filtration. It involves the addition of calculated quantities of lime $\text{Ca}(\text{OH})_2$ and soda Na_2CO_3 . The hardness

causing impurities react with these chemicals forming precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$. These precipitates are then filtered off to obtain soft water.

The precipitates formed are very fine and do not settle easily causing difficulty in filtration. Therefore small amount of coagulants like alum ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$), ferrous sulphate (FeSO_4) or sodium aluminate (NaAlO_2) are added. They help in the quick setting of precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$ by the process of loading.

(The coagulants hydrolyse to form $\text{Al}(\text{OH})_3$ which entraps the fine precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$. The precipitates become heavy and settle fast. This process is called loading).

Calculation of Lime-Soda Requirement

Calculated quantity of lime and soda are added to hard water to remove temporary and permanent hardness. These chemicals also react with CO_2 , H_2S gas, free mineral acids present in water and also with the coagulants added in water.

Table 2.8 Chemical reactions involved in lime soda process and calculation of the requirement of lime and soda for water softening

Constituent	Reaction	Requirement of lime/soda	Explanation
$\text{Ca}(\text{HCO}_3)_2$, CaCO_3 (temporary Ca hardness)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	L	One equivalent of $\text{Ca}(\text{HCO}_3)_2$ is removed by one equivalent of lime, hence the requirement is L
$\text{Mg}(\text{HCO}_3)_2$, MgCO_3 (temporary Mg hardness)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 \downarrow + 2\text{H}_2\text{O}$ The reaction occurs in two steps $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{MgCO}_3 \downarrow + \text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$ MgCO_3 is fairly soluble and reacts further $\text{MgCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{CaCO}_3$	2L	Removal of one equivalent of $\text{Mg}(\text{HCO}_3)_2$ requires 2 equivalent of lime hence 2L
Ca^{2+} [CaCl_2 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$] permanent Ca^{2+} hardness	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	S	One equivalent of Ca^{2+} is removed by one equivalent of soda hence requirement is S
Mg^{2+} [MgCl_2 , MgSO_4 , $\text{Mg}(\text{NO}_3)_2$] permanent Mg^{2+} hardness	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	L+S	Lime removes permanent Mg^{2+} hardness but introduces Ca^{2+} hardness which is removed by soda
HCO_3^- (e.g., NaHCO_3)	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-}$ or $2\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L-S	Bicarbonate present in water consumes equivalent amount of lime and equivalent amount of soda is produced which is to be subtracted from total soda requirement

CO ₂	CO ₂ + Ca(OH) ₂ → CaCO ₃ + H ₂ O	L	One equivalent of CO ₂ is removed by one equivalent of lime
H ₂ S	H ₂ S + Ca(OH) ₂ → CaS + H ₂ O	L	Does not produce hardness but consumes equivalent amount of lime and hence is to be considered for calculation
H ⁺ (Free acids like HCl, H ₂ SO ₄)	2H ⁺ + Ca(OH) ₂ → Ca ²⁺ + 2H ₂ O Ca ²⁺ + Na ₂ CO ₃ → CaCO ₃ + 2Na ⁺	L + S	Free acids present in water react with lime introducing Ca ²⁺ hardness in water which is in turn removed by soda
(Coagulant) FeSO ₄	Fe ²⁺ + Ca(OH) ₂ → Fe(OH) ₂ + Ca ²⁺ 2Fe(OH) ₂ + H ₂ O + O ₂ → 2Fe(OH) ₃ Ca ²⁺ + Na ₂ CO ₃ → CaCO ₃ + 2Na ⁺	L + S	FeSO ₄ coagulants added to remove hardness reacts with equivalent amount of lime producing Ca ²⁺ which are removed by soda. Hence it is to be considered while calculating lime-soda requirement
Al ₂ (SO ₄) ₃	2Al ³⁺ + 3Ca(OH) ₂ → 2Al(OH) ₃ + 3Ca ²⁺ 3Ca ²⁺ + 2Na ₂ CO ₃ → 3CaCO ₃ + 6Na ⁺	L + S	FeSO ₄ coagulants added to remove hardness react with equivalent amount of lime producing Ca ²⁺ which are removed by soda. Hence it is to be considered while calculating lime-soda requirement
NaAlO ₂	NaAlO ₂ + 2H ₂ O → NaOH + Al(OH) ₃	–L	On hydrolysis NaAlO ₂ gives NaOH which is considered as 1 equivalent of Ca(OH) ₂ hence the amount of lime formed is to be subtracted from total lime requirement

Lime Requirement

Since 100 parts by mass of CaCO₃ are equivalent to 74 parts by mass of Ca(OH)₂

∴ Lime required for softening

$$= \frac{74}{100} (\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Permanent Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}_2\text{S} + \text{Free acids} +$$

FeSO₄ + Al₂(SO₄)₃ – NaAlO₂ all in terms of CaCO₃ equivalent)

Soda Requirement

100 parts of CaCO₃ are equivalent to 106 parts of Na₂CO₃

$$= \frac{106}{100} (\text{Perm Ca}^{2+} + \text{Permanent Mg}^{2+} - \text{HCO}_3^- + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 \text{ all in}$$

terms of CaCO₃ equivalent)

Note The above calculation gives lime and soda requirement for one liter water. The total lime/soda requirement for V liters water is calculated by multiplying volume of water in the above two formulas.

If lime and soda is impure

Say purity of lime = 90%

Purity of soda = 95%

Then lime required to soften water

$$= \frac{74}{100} (\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Permanent Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}_2\text{S} + \text{Free acids} +$$

$$\text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{NaAlO}_2 \text{ all in terms of CaCO}_3 \text{ equivalent}) \times \text{vol of water} \times \frac{100}{\% \text{ purity}}$$

$$\text{Lime} = \frac{74}{100} (\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Permanent Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}_2\text{S} + \text{Free acids} +$$

$$\text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{NaAlO}_2 \text{ all in terms of CaCO}_3 \text{ equivalent}) \times \text{Vol of water} \times \frac{100}{90}$$

Similarly, soda required—

$$= \frac{106}{100} (\text{Perm Ca}^{2+} + \text{Permanent Mg}^{2+} - \text{HCO}_3^- + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 \text{ all in}$$

$$\text{terms of CaCO}_3 \text{ equivalent}) \times \text{vol of water} \times \frac{100}{\% \text{ purity}}$$

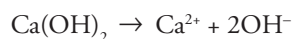
$$= \frac{106}{100} (\text{Perm Ca}^{2+} + \text{Permanent Mg}^{2+} - \text{HCO}_3^- + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 \text{ all in}$$

$$\text{terms of CaCO}_3 \text{ equivalent}) \times \text{Vol of water} \times \frac{100}{95}$$

If the treated water contains excess of OH^- and CO_3^{2-} ions, it implies that excess soda and lime has been added.

Reaction involved in giving excess OH^- and CO_3^{2-}

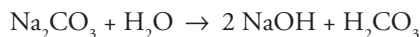
Excess OH^- comes from excess lime added in water



Hence if treated water contains excess OH^- then lime requirement

$$= \frac{74}{100} (\text{Temp Ca}^{2+} + 2 \times \text{Temp Mg}^{2+} + \text{Permanent Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}_2\text{S} + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 - \text{NaAlO}_2 + \text{OH}^- \text{ as CaCO}_3 \text{ equivalent}).$$

Similarly excess Na_2CO_3 contributes to both excess OH^- and excess CO_3^{2-} in treated water and hence both are to be added for soda calculation:

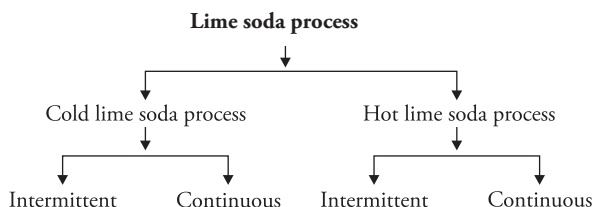


$$= \frac{106}{100} (\text{Perm Ca}^{2+} + \text{Permanent Mg}^{2+} - \text{HCO}_3^- + \text{Free acids} + \text{FeSO}_4 + \text{Al}_2(\text{SO}_4)_3 + \text{OH}^- + \text{CO}_3^{2-} \text{ all in terms of CaCO}_3 \text{ equivalent}).$$

NOTES

1. Substances like KCl, SiO_2 , Fe_2O_3 and Na_2SO_4 do not impart any hardness and therefore they do not consume any soda and lime therefore these should not be considered while calculating soda and lime.
2. When impurities are given as CaCO_3 or MgCO_3 these should be considered as temporary hardness due to bicarbonates.

PROCESS



1. Cold intermittent lime soda process

It is also called batch process. It consists of a tank which has an inlet for raw water and chemicals, outlet for softened water and sludge and a mechanical stirrer (Fig. 2.2). Calculated quantities of lime, soda and coagulant are added through the chemical feed inlet and raw water is added through another inlet simultaneously, and these are mixed thoroughly with the help of stirrer. For accelerating the process some sludge, (from previous operation) is added which acts as nucleus for fresh precipitation. The sludge (precipitate) formed is allowed to settle down, and is then removed through the sludge outlet. The softened water is removed through a floating pipe and sent to the filtering unit. Later when lot of sludge is collected the process has to be stopped to remove the sludge. This problem can be solved by using a set of

tanks. Using a set of tanks ensures continuous supply of soft water by planned alternate cycle of reaction and settling.

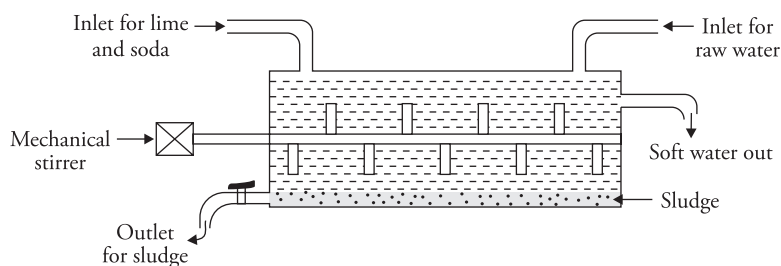


Figure 2.2 Cold intermittent lime soda process

2. Cold continuous lime soda process

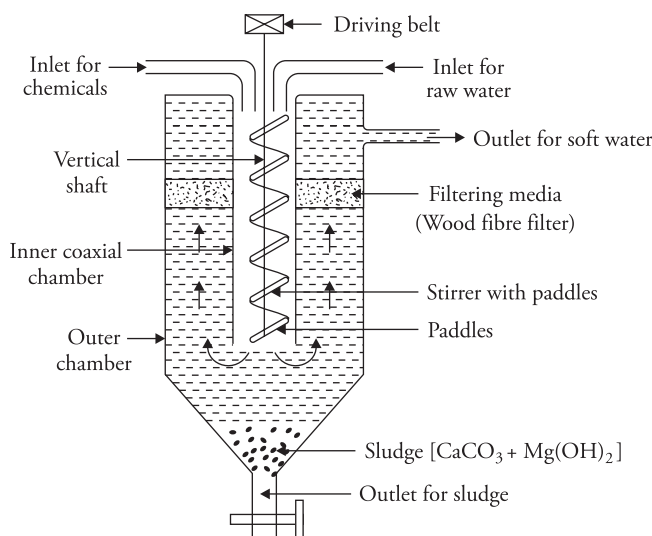


Figure 2.3 Cold continuous lime soda process

Apparatus It consists of two concentric vertical co-axial chambers. The inner tank is open from the bottom and has an inlet for chemicals (lime, soda and coagulants) and for hard water at the upper end. It is also provided with a stirrer with paddle plates. The outer chamber has a sludge outlet at the bottom and an outlet for soft water near the top. Just below the soft water outlet is the wood fibre filter for the filtration of soft water (Fig. 2.3).

Process Hard water is first analysed and then calculated quantity of chemicals and raw water are added simultaneously in the inner chamber. Vigorous stirring ensures continuous mixing of raw material and water. Softening of water occurs. The sludge thus formed settles down. Soft water rises up, passes through the wood fibre filter where traces of sludge are removed. Filtered soft water is then collected from the outlet near the top.

Sludge can be removed from the bottom from time to time. The cold lime soda process is not used these days for softening of boiler feed water because the water thus obtained has high residual hardness. This residual hardness harms the tubes in the boilers.

3. **Hot intermittent lime-soda process**

It is similar to the intermittent type cold lime-soda softener except that the heating coils are installed in it for heating water.

4. **Hot continuous lime-soda process** It is similar to cold lime-soda process except that the raw water and chemicals are heated to a temperature of 80–150°C.

The apparatus consists of three parts (Fig. 2.4):

- (a) **Reaction tank** It has three separate inlets, one each for raw water, chemicals and superheated steam. All these are thoroughly mixed inside the reaction tank where the chemical reaction occurs forming insoluble precipitates of CaCO_3 and $\text{Mg}(\text{OH})_2$ which settle down as sludge.
- (b) **Sedimentation tank** From the reaction tank the contents go to this tank. The sludge settles down and the water rises up and enters the sandfilter.
- (c) **Sand filter** It has layers of fine and coarse sand which acts as filter and ensures complete removal of sludge from the softened water.

Process

All the raw materials are put in through the three inlets in the reaction chamber. Here thorough mixing of raw materials takes place in the presence of superheated steam. Sludges settle down at the conical mouth of vertical outer chamber and 'sand filter' is provided for filtration to ensure complete removal of sludge from softened water giving finally filtered softened water.

Advantages of hot lime-soda process

1. Rate of reaction increases. The process is completed in 15 minutes whereas cold lime-soda process takes several hours for completion.
2. High temperature accelerates the chemical reactions. The rate of settling and filtration also increases. Thus the softening capacity of the hot process is several times higher than the cold process.
3. No coagulant is required.
4. Lesser quantity of chemicals are required.
5. Dissolved gases like CO_2 and H_2S are expelled out.
6. Viscosity of water decreases hence filtration becomes easier.
7. The residual hardness in softened water is 15–30 ppm, which is less than that of water received from cold lime-soda process (upto 60 ppm).
8. The precipitate formed is larger, coarser, heavier and settles rapidly. Most important advantage is that the silica in water is also removed in this process. Dissolved silica in water is absorbed or reacts at the surface of each precipitated particle of $\text{Mg}(\text{OH})_2$.

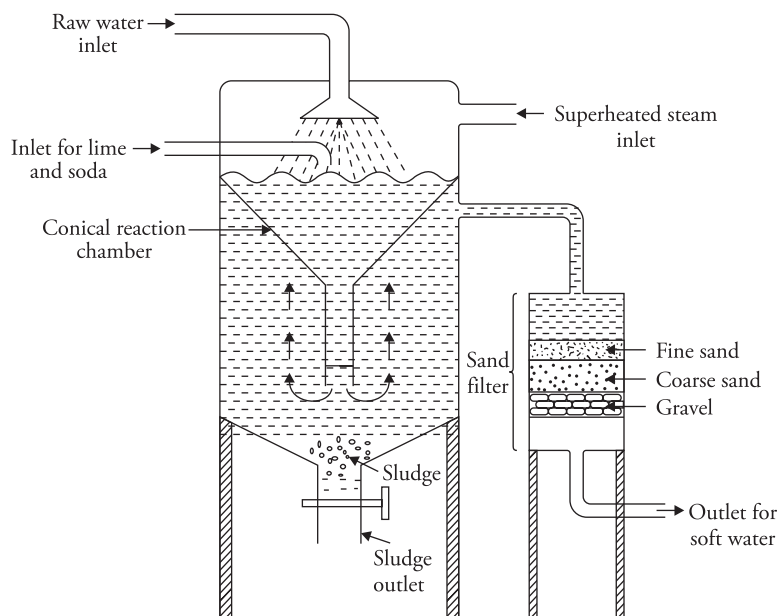


Figure 2.4 *Hot continuous lime soda process*

Merits of lime-soda process

1. Very economical.
2. During softening, the treated water has pH >7; hence it is alkaline and therefore has less corrosion tendencies.
3. Alkaline nature of softened water prevents the growth of bacteria.
4. Fe, Mn and dissolved minerals are also reduced in this process.

Demerits of the process

1. Requires careful and skilled supervision.
2. Sludge disposal is a problem.
3. It can remove hardness only up to 15 ppm which is still not appropriate for boilers.
4. The softened water contains appreciable amount of soluble salts such as sodium sulphate and cannot be used in high pressure boilers.
5. It cannot be used in households as it is not possible to calculate the amount of lime and soda required.

Solved Examples

1. Calculate the amount of lime required for softening 50,000 liters of hard water containing; $\text{CaCO}_3 = 25$ ppm; $\text{MgCO}_3 = 144$ ppm; $\text{CaCl}_2 = 111$ ppm; $\text{MgCl}_2 = 95$ ppm; $\text{Na}_2\text{SO}_4 = 15$ ppm; $\text{Fe}_2\text{O}_3 = 25$ ppm.

Solution

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
CaCO_3	25 ppm	$\frac{25 \times 100 / 2}{100 / 2} = 25$ ppm	L
MgCO_3	144 ppm	$\frac{144 \times 100 / 2}{84 / 2} = 171.43$ ppm	2L
CaCl_2	111 ppm	$\frac{111 \times 100 / 2}{111 / 2} = 100$ ppm	S
MgCl_2	95 ppm	$\frac{95 \times 100 / 2}{95 / 2} = 100$ ppm	L + S
Na_2SO_4	15 ppm	Does not impart hardness	
Fe_2O_3	25 ppm	Does not impart hardness	

Lime required for softening 50,000 liters of hard water

$$= \frac{74}{100} [\text{CaCO}_3 + 2 \times \text{MgCO}_3 + \text{MgCl}_2 \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water.}$$

$$= \frac{74}{100} [25 + 2 \times 171.43 + 100] \text{ mg/L} \times 50,000 \text{ L}$$

$$= \frac{74}{100} [467.86] \text{ mg/L} \times 50,000 \text{ L} = 1,73,10,820 \text{ mg} = 17.311 \text{ kg} \quad (1 \text{ kg} = 10^6 \text{ mg})$$

Lime Required = 17.311 kg

(Hardness expressed as CaCO_3 and MgCO_3 is treated as temporary hardness)

2. A water sample contains the following impurities

$\text{Ca}^{2+} = 20$ ppm; $\text{Mg}^{2+} = 18$ ppm; $\text{HCO}_3^- = 183$ ppm; $\text{SO}_4^{2-} = 24$ ppm. Calculate the amount of lime and soda needed for softening.

Solution

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
Ca^{2+}	20 ppm	$\frac{20 \times 100 / 2}{40 / 2} = 50 \text{ mg/L}$	S
Mg^{2+}	18 ppm	$\frac{18 \times 100 / 2}{24 / 2} = 75 \text{ mg/L}$	L+S
HCO_3^-	183 ppm	$\frac{183 \times 100 / 2}{61 / 1} = 150 \text{ mg/L}$	L-S
SO_4^{2-}	24 ppm	—	—

As the volume of water is not given in the question hence calculations may be done for one liter water.

Lime required

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{74}{100} [75 + 150] \times 1$$

$$= \frac{74}{100} [225] \times 1 = 166.5 \text{ mg}$$

$$\text{Lime} = 166.5 \text{ mg}$$

Soda requirement

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{106}{100} [50 + 75 - 150] \times 1$$

$$= \frac{106}{100} [-25] = -26.50 \text{ mg}$$

The answer is negative, which shows that soda formed from bicarbonate is more than the amount of soda required for the removal of various impurities. Hence, the amount of soda to be added will be zero. **Soda = Nil**

3. Calculate the amount of lime and soda required for softening 18,000 liters of water, which is analysed as follows:

Temporary hardness = 25 ppm

Permanent hardness = 20 ppm

Permanent Mg hardness = 15 ppm

Solution

Temporary hardness is due to $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ and lime is required to remove both.

For removal of permanent hardness

Due to Mg – Lime + soda is required

Due to Ca – Only soda is required

∴ to calculate the total lime requirement we add –Temporary hardness + Permanent Mg hardness and to calculate soda requirement only total permanent hardness is considered.

Lime required

$$= \frac{74}{100} [\text{Temporary hardness} + \text{Permanent Mg hardness}] \times \text{Volume of water}$$

$$= \frac{74}{100} [25 + 15] \times 18000$$

$$= \frac{74}{100} [40] \times 18000 = 532800 \text{ mg} = 532.8 \text{ g}$$

$$\text{Lime} = 532.8 \text{ g}$$

Soda Requirement

$$\frac{106}{100} [\text{Permanent hardness}] \times \text{Volume of water}$$

$$\frac{106}{100} [20 \text{ ppm}] \times 18000 = 381600 \text{ mg} = 381.6 \text{ g}$$

$$\text{Soda} = 381.6 \text{ g}$$

4. A sample of water on analysis was found to contain the following in mg/L

$\text{CaSO}_4 = 0.45$; $\text{MgCO}_3 = 0.50$; $\text{CaCO}_3 = 2.50$; $\text{MgSO}_4 = 0.85$; $\text{MgCl}_2 = 0.80$; $\text{SiO}_2 = 2.90$; $\text{NaCl} = 2.80$.

Calculate the amount of lime and soda required to soften 25,000 liters of water per day for a year if the purity of lime and soda is 90%.

Solution

Conversion into equivalents of CaCO_3

Constituent	Amount(mg/L)	Equivalents of CaCO_3	Requirement L/S
CaSO_4	0.45	$\frac{0.45 \times 100 / 2}{136 / 2} = 0.3309$	S
MgCO_3	0.50	$\frac{0.50 \times 100 / 2}{84 / 2} = 0.595$	2L
CaCO_3	2.50	$\frac{2.50 \times 100 / 2}{100 / 2} = 2.5$	L
MgSO_4	0.85	$\frac{0.85 \times 100 / 2}{120 / 2} = 0.708$	L + S
MgCl_2	0.80	$\frac{0.80 \times 100 / 2}{95 / 2} = 0.842$	L + S
SiO_2	2.90	Does not impart hardness and does not consume lime and soda	
NaCl	2.80	Does not impart hardness and does not consume lime and soda	

Volume of water = 25,000 liters a day for a year.

\therefore Total volume of water to be softened = 25000×365 days

Purity of lime and soda = 90%

Lime required

$$= \frac{74}{100} [2 \times \text{MgCO}_3 + \text{CaCO}_3 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water}$$

$$= \frac{74}{100} [2 \times 0.595 + 2.5 + 0.708 + 0.8421] \times 25000 \times 365$$

$$= 35383100 \text{ mg}$$

The above result is for lime of 100% purity. However, lime in question is 90% pure. This means that when 90 mg lime is required 100 mg of lime is to be added to water.

Hence lime actually added = $35383100 \times \frac{100}{90}$ mg = 39314555.56 mg = 39.31 kg

Lime added = 39.31 kg

Similarly soda can also be calculated using the same analogy

Soda Requirement

$$= \frac{106}{100} [\text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [0.3309 + 0.708 + 0.842] \times 25000 \times 365 \times \frac{100}{90}$$

$$= \frac{106}{100} [1.8809] \times 25000 \times 365 \times \frac{100}{90} = 20214450.28 \text{ mg} = 20.214 \text{ kg.}$$

5. Calculate the amount of lime and soda needed for softening 100000 liters of water containing the following:

HCl = 8.9 mg/L; $\text{Al}_2(\text{SO}_4)_3$ = 38.9 mg/L; MgCl_2 = 10.2 mg/L; NaCl = 30.38 mg/L

Purity of lime is 90% and that of soda is 98%. Ten percent chemicals are to be used in excess in order to complete the reaction quickly.

Solution

Conversion into equivalents of CaCO_3

Constituent	Amount(mg/L)	Equivalents of CaCO_3	Requirement L/S
HCl	8.9 mg/L	$\frac{8.9 \times 100 / 2}{36.5 / 1} = 12.191$	L + S
$\text{Al}_2(\text{SO}_4)_3$	38.9 mg/L	$\frac{38.9 \times 100 / 2}{342 / 6} = 34.12$	L + S
MgCl_2	10.2 mg/L	$\frac{10.2 \times 100 / 2}{95 / 2} = 10.737$	L + S
NaCl	30.38 mg/L	Does not impart hardness	

Volume of water = 10^5 liter

Purity of lime = 90%; Purity of soda = 98%

10% chemicals are to be used in excess in order to complete the reaction quickly.

Lime required

$$\begin{aligned}
 &= \frac{74}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}} \\
 &= \frac{74}{100} [12.191 + 34.12 + 10.737] \times 10^5 \times \frac{100}{90} \\
 &= \frac{74}{100} [57.048 \text{ mg/L}] \times 10^5 \times \frac{100}{90} = 4.6906 \times 10^6 \text{ mg}
 \end{aligned}$$

Since, 10% chemicals are used in excess

∴ Lime actually added

$$4.6906 \times 10^6 \times \frac{110}{100} = 5.159 \times 10^6 \text{ mg} = 5.159 \text{ kg}$$

Lime added = 5.159 kg

Soda requirement

$$\begin{aligned}
 &= \frac{106}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}} \\
 &= \frac{106}{100} [12.191 + 34.12 + 10.737] \times 10^5 \times \frac{100}{98} \\
 &= \frac{106}{100} \times 57.048 \times 10^5 \times \frac{100}{98} = 6.1704 \times 10^6 \text{ mg} = 6.1704 \text{ kg}
 \end{aligned}$$

$$\text{Soda added (considering 10\% excess)} = 6.1704 \times \frac{110}{100} = 6.787 \text{ kg}$$

Soda added = 6.787 kg

6. A water works has to supply 1 m³/s of water. Raw water contains:

Mg(HCO₃)₂ = 219 ppm; Mg²⁺ = 36 ppm; HCO₃⁻ = 18.3 ppm; H⁺ = 1.5 ppm. Calculate the cost of treating water per day, if lime (90% pure) and soda (95% pure) cost Rs. 500 per ton and Rs. 7000 per ton, respectively.

SolutionConversion into equivalents of CaCO_3

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
$\text{Mg}(\text{HCO}_3)_2$	219 ppm	$\frac{219 \times 100 / 2}{146 / 2} = 150 \text{ ppm}$	2L
Mg^{2+}	36 ppm	$\frac{36 \times 100 / 2}{24 / 2} = 150 \text{ ppm}$	L+S
HCO_3^-	18.3 ppm	$\frac{18.3 \times 100 / 2}{61 / 1} = 15 \text{ ppm}$	L - S
H^+	1.5 ppm	$\frac{1.5 \times 100 / 2}{1 / 1} = 75 \text{ ppm}$	L + S

Purity of lime = 90%; Purity of soda = 95%

Volume of water to be purified in 24 hours

$$(1 \text{ m}^3/\text{s}) \times (60 \times 60 \times 24) = 86400 \text{ m}^3/\text{day} = 8.64 \times 10^7 \text{ L} \quad (1 \text{ m}^3 = 1000 \text{ liters})$$

Lime required

$$= \frac{74}{100} [2 \times \text{Mg}(\text{HCO}_3)_2 + \text{Mg}^{2+} + \text{HCO}_3^- + \text{H}^+ \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{74}{100} [2 \times 150 + 150 + 15 + 75] \times 8.64 \times 10^7 \times \frac{100}{90}$$

$$= \frac{74}{100} [540] \times 8.64 \times 10^7 \times \frac{100}{90} = 3836.16 \times 10^7 \text{ mg} = 38.36 \text{ tons} \quad (1 \text{ ton} = 10^3 \text{ kg} = 10^9 \text{ mg})$$

Lime = 38.36 tons

Soda requirement

$$= \frac{106}{100} [\text{Mg}^{2+} - \text{HCO}_3^- + \text{H}^+ \text{ as } \text{CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [150 + 75 - 15] \times 8.64 \times 10^7 \times \frac{100}{95}$$

$$= \frac{106}{100} [210] \times 8.64 \times 10^7 \times \frac{100}{95} = 2024.48 \times 10^7 \text{ mg} = 20.24 \text{ tons}$$

Soda = 20.24 tons

Cost of lime = Rs. 500 per ton

Cost of soda = Rs. 7000 per ton

Total cost of treating water per day = $(38.36 \times 500 + 20.24 \times 7000)$

= 19180 + 141680 = Rs. 1,60,860

Ans = Rs. 1,60,860

7. Calculate the amount of lime and soda required for softening 30,000 liters of hard water, which is analysed as follows:

Analysis of raw water

Ca^{2+} = 400 ppm; Mg^{2+} = 288 ppm; HCO_3^- = 1586 ppm; dissolved CO_2 = 88 ppm;

Ferrous sulphate = 139 ppm (commercial grade)

Analysis of treated water

CO_3^{2-} = 30 ppm; OH^- = 34 ppm

Purity of lime is 94% and that of soda is 86%.

Solution

Conversion into equivalents of CaCO_3

Constituent	Amount	Equivalents of CaCO_3	Requirement L/S
Analysis of raw water			
Ca^{2+}	400 ppm	$\frac{400 \times 100 / 2}{40 / 2} = 1000 \text{ ppm}$	S
Mg^{2+}	288 ppm	$\frac{288 \times 100 / 2}{24 / 2} = 1200 \text{ ppm}$	L + S
CO_2	88 ppm	$\frac{88 \times 100 / 2}{44 / 2} = 200 \text{ ppm}$	L
HCO_3^-	1586 ppm	$\frac{1586 \times 100 / 2}{61 / 1} = 1300 \text{ ppm}$	L – S

Ferrous sulphate (commercial grade)	139 ppm	$\frac{139 \times 100 / 2}{278 / 2} = 50 \text{ ppm}$	L + S
Analysis of treated water			
OH ⁻	34 ppm	$\frac{34 \times 100 / 2}{17 / 1} = 100 \text{ ppm}$	L + S
CO ₃ ²⁻	30 ppm	$\frac{30 \times 100 / 2}{60 / 2} = 50 \text{ ppm}$	S

Volume of water = 30,000 liters

Purity of lime = 94%; purity of soda = 86%

Lime required

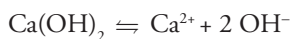
$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{74}{100} [1200 + 1300 + 200 + 50] \times 30,000 \times \frac{100}{94}$$

$$= \frac{74}{100} [2750] \times 30,000 \times \frac{100}{94} = 64946809 \text{ mg} = 64.95 \text{ kg}$$

$$\text{Lime} = 64.95 \text{ kg}$$

The excess lime added for treatment of water gives OH⁻ ions in treated water



∴ Excess lime added

$$= \frac{74}{100} [\text{OH}^- \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{74}{100} [100] \times 30,000 \times \frac{100}{94} = 2361702.1 \text{ mg} = 2.362 \text{ kg}$$

$$\text{Total lime} = 64.95 + 2.362 = 67.312 \text{ kg}$$

Soda Requirement

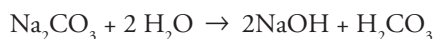
$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{FeSO}_4 \cdot 7\text{H}_2\text{O as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [1000 + 1200 - 1300 + 50] \times 30,000 \times \frac{100}{86}$$

$$= \frac{106}{100} [950] \times 30,000 \times \frac{100}{86} = 35127907 \text{ mg} = 35.128 \text{ kg}$$

$$\text{Soda} = 35.128 \text{ kg}$$

The excess soda added during softening process contributes to both CO_3^{2-} and OH^- in treated water.



Excess soda added

$$= \frac{106}{100} [\text{OH}^- + \text{CO}_3^{2-} \text{ as CaCO}_3 \text{ equivalent}] \times \text{Volume of water} \times \frac{100}{\% \text{ purity}}$$

$$= \frac{106}{100} [100 + 50] \times 30,000 \times \frac{100}{86} = \frac{106}{100} [150] \times 30,000 \times \frac{100}{86}$$

$$5546511.6 \text{ mg} = 5.546 \text{ kg}$$

$$\text{Total soda} = 35.128 + 5.546 = 40.674 \text{ kg}$$

Practice Problems

1. Calculate the amount of lime required for softening 50,000 liters of hard water containing $\text{CaCO}_3 = 20 \text{ ppm}$; $\text{MgCO}_3 = 190 \text{ ppm}$; $\text{CaCl}_2 = 120 \text{ ppm}$; $\text{MgCl}_2 = 100 \text{ ppm}$; $\text{Na}_2\text{SO}_4 = 20 \text{ ppm}$; $\text{Fe}_2\text{O}_3 = 30 \text{ ppm}$.
[Ans Lime required = 21.37 kg]
2. A sample of water was analysed and found to contain temporary magnesium hardness = 25 mg/L; permanent magnesium chloride hardness = 15 mg/L; permanent calcium sulphate hardness = 20 mg/L and $\text{SiO}_2 = 300 \text{ mg/L}$. Calculate the lime and soda required for softening 30,000 liters of hard water.

$$[\text{Ans Lime} = 1.1107 \text{ kg; Soda} = 0.9699 \text{ kg}]$$

3. Calculate the quantities of lime and soda required for softening 3,00,000 liters of water using 164 ppm of sodium aluminate as coagulant. The analytical result of raw water is

$\text{Ca}^{2+} = 240 \text{ ppm}$; $\text{Mg}^{2+} = 96 \text{ ppm}$; $\text{HCO}_3^- = 732 \text{ ppm}$; $\text{CO}_2(\text{dissolved}) = 44 \text{ ppm}$; $\text{NaCl} = 60 \text{ ppm}$; $\text{Fe}_2\text{O}_3 = 160 \text{ ppm}$.

[Ans Lime = 222 kg; soda = 127.2 kg]

4. Calculate the quantity of lime and soda required to soften 25000 gallons of hard water containing $\text{Ca}(\text{HCO}_3)_2 = 20$ grains; $\text{Mg}(\text{HCO}_3)_2 = 15$ grains; $\text{CaSO}_4 = 5$ grains by lime soda process.

[Ans Lime = 86.9 lbs (pounds); Soda = 13.93 lbs(pound)]

5. Calculate the quantity of lime and soda required for softening 60,000 liters of hard water. The analysis is as follows:

Temporary hardness = 55.5 ppm

Permanent calcium hardness = 42.5 ppm

Permanent magnesium hardness = 48 ppm

[Ans Lime = 4.60 kg; Soda = 5.76 kg]

6. Calculate the amount of lime (90% pure) and soda (98% pure) required for the treatment of one million liters of water containing

$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ ppm}$; $\text{CaCl}_2 = 33.3 \text{ ppm}$; $\text{HCO}_3^- = 91.5 \text{ ppm}$; $\text{MgCl}_2 = 38 \text{ ppm}$; $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$. The coagulant $\text{Al}_2(\text{SO}_4)_3$ was added at a rate of 17.1 mg/L of water.

[Ans Lime = 127.44 kg; Soda = 10.82 kg]

7. A sample of water on analysis gave the following results:

$\text{H}_2\text{SO}_4 = 147 \text{ mg/L}$; $\text{MgCl}_2 = 95 \text{ mg/L}$; $\text{MgSO}_4 = 24 \text{ mg/L}$; $\text{CaSO}_4 = 170 \text{ mg/L}$ and $\text{KCl} = 20 \text{ mg/L}$.

Water is to be supplied to the town of the population of one lakh only. The daily consumption of water is 100 liters per head. Calculate the cost of lime and soda required for softening hard water for the town for one month (November). If lime is 90% pure and Rs. 5 per kg and soda is 92% pure and costs Rs. 8.00 per kg.

[Ans Cost of lime = Rs 3,33,000; Cost of soda = Rs. 1092260.87]

8. Calculate the amount of lime and soda needed for softening 75,000 liters of hard water. The results of analysis of raw water and treated water are as follows:

Analysis of raw water

$\text{HCO}_3^- = 212 \text{ mg/L}$; $\text{H}^+ = 3 \text{ mg/L}$; $\text{Ca}^{2+} = 55.5 \text{ mg/L}$; $\text{Mg}^{2+} = 42 \text{ mg/L}$; $\text{CO}_2 = 66 \text{ mg/L}$;

Analysis of treated water

$\text{CO}_3^{2-} = 90 \text{ mg/L}$; $\text{OH}^- = 45 \text{ mg/L}$.

In this treatment, 20 mg/L of NaAlO_2 was used as a coagulant.

[Ans Total Lime = 42.67 kg; Total Soda = 45.5 kg]

Zeolite or Permutit Process

Zeolites are also known as permutit and in Greek it means 'boiling stone'.

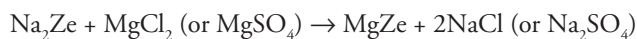
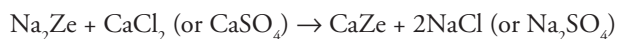
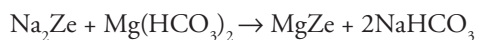
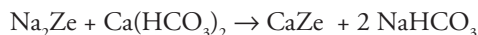
They occur naturally as hydrated alumino silicate minerals like $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$ where $x = 2-10$ and y is $2-6$. They are capable of exchanging reversibly sodium ions for hardness producing ions in water.

Zeolites are of two types

1. *Natural Zeolites* Non porous, amorphous and durable, for example, Natrolite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
2. *Synthetic Zeolites* Porous with gel-like structure. They are prepared by heating sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2).

Process Hard water is percolated at a specified rate through a bed of zeolite stacked in a cylindrical unit as shown in the diagram (Fig. 2.5). The hardness causing elements (Ca^{2+} , Mg^{2+} etc) are retained by zeolite as CaZe and MgZe , while the outgoing water contains sodium salts.

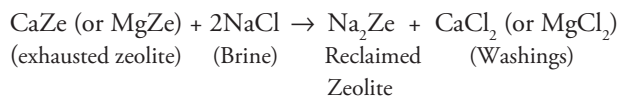
The chemical reactions involved are



After some time, all the sodium ions in zeolite are replaced by Ca and Mg ions giving CaZe/MgZe . Such a zeolite bed is unable to soften water further and is said to be exhausted. It has to be regenerated to enable it to soften water again. It may be noted that the water obtained by zeolite process is used mostly for laundry purpose; it cannot be used in boilers.

Regeneration

When the zeolite bed is exhausted the supply of hard water is stopped and it is regenerated by treating with a concentrated brine (10% NaCl) solution.



The washings (containing CaCl_2 , MgCl_2 , etc.) are led to drain and the regenerated zeolite bed is used again for softening. (NaNO_3 , KCl , KNO_3 , etc. can also be used for regeneration instead of

NaCl, but NaCl is mostly used because of its low cost and the products of regeneration process (CaCl_2 or MgCl_2) are highly soluble and can be easily rinsed out of the zeolite bed).

By knowing the amount of NaCl used for regeneration of the exhausted zeolite bed, the hardness of the water sample can be calculated by using the formula.

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

where

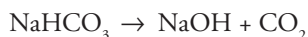
V_1 = Total volume of water softened

V_2 = Total volume of NaCl solution used for regeneration

m = Amount of NaCl in g/L present in V_2

Limitations and Disadvantages of Zeolite Process

1. If the water supplied is turbid, the turbidity/suspended matter is to be removed (by coagulation, filtration, etc.) before the water is admitted to the zeolite bed otherwise turbidity will clog the pores of zeolite bed making it inactive.
2. If the water contains ions like Mn^{2+} and Fe^{2+} , they must be removed first because these ions react with zeolite bed to give manganese and iron zeolites which cannot be easily regenerated.
3. Minerals acids, if present in water, destroy the zeolite bed and hence they must be neutralised with soda in advance, before feeding water into the zeolite bed.
4. This method does not remove anions. The bicarbonates present in hard water get converted into NaHCO_3 which goes into soft water effluent. If this water is used in boiler, NaHCO_3 dissociates as



NaOH leads to caustic embrittlement and CO_2 makes the water acidic and corrosive.

5. The treated water contains more sodium salts than in lime-soda process.
6. Moreover high cost of the plant and material also acts as limiting factor.

Advantages of Zeolite Process

1. Hardness is removed almost completely and the residual hardness is about 10 ppm.
2. The equipment is compact and occupies less space.
3. It is a clean and rapid process. Sludge is not formed as the impurities are not precipitated.
4. It requires less skill for maintenance as well as operation.

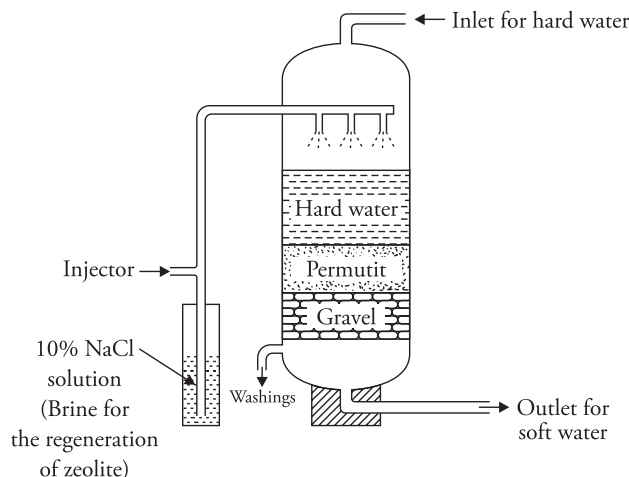


Figure 2.5 Zeolite process

Table 2.9 Comparison of Permutit Process with Lime-Soda Process

S.No	Zeolite/Permutit Process	Lime-Soda Process
1	Residual hardness of water obtained is 10-15 ppm	Water of generally 15-50 ppm residual hardness is obtained
2	Cost of plant and zeolite are higher i.e capital cost is high	Capital cost is lower
3	Operation expenses are low as cheap NaCl is required for regeneration	Operation expenses high as costly chemicals (lime, soda and coagulants) are consumed
4	Occupies less space as it is compact	Plant occupies more space as it depends on the amount of water to be softened
5	It cannot be used for treating acidic water, because the zeolite undergoes disintegration	There is no such limitation
6	The treated water contains large amount of sodium salts than in original raw water. The NaHCO_3 in treated water causes caustic embrittlement	Treated water contains lesser % of sodium salts. It is completely free from NaHCO_3 as it is removed in the form of insoluble CaCO_3 and Mg(OH)_2
7	Raw water to be softened, must be free from suspended matter, otherwise the pores of zeolite block and the bed loses its ion exchange capacity	The process is free from such limitation
8	It can be operated under pressure and can be designed for fully automatic operation	This process cannot be operated under pressure.
9	It is clean process as no sludge is formed	Large amount of sludge is formed
10	Control test comprises in checking the hardness of treated water. The process adjusts itself to water of different hardness	In order to meet the changing hardness of incoming water frequent control and adjustment of reagents is needed

Solved Examples

1. A zeolite softener was used to remove the hardness of 95,000 liters of hard water completely. The softener required 475 liters of NaCl solution containing 18 g/liter of NaCl for regeneration. Calculate the hardness of hard water in ppm.

Solution

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

V_1 = Total volume of water softened = 95,000 liters

V_2 = Total volume of NaCl solution used for regeneration = 475 liters

m = Amount of NaCl present in V_2 = 18 g

$$\text{Hardness (H)} = \frac{50 \times 18 \times 475 \times 10^3}{58.5 \times 95,000} = 76.92 \text{ ppm}$$

Hardness (H) = 76.92 ppm

2. An exhausted zeolite softener was regenerated by 325 liters of NaCl solution containing 60 g/liter of NaCl. How many liters of hard water of hardness 250 mg/L can be softened by the zeolite softener.

Solution

Given

V_1 = Total volume of water softened = ?

V_2 = Total volume of NaCl solution used for regeneration = 325 liters

m = Amount of NaCl present in V_2 = 60 g/liter

Hardness (H) = 250 mg/liter = 250 ppm

Formula

$$\text{Hardness (H)} = \frac{50 \times m \times V_2 \times 10^3}{58.5 \times V_1}$$

$$250 = \frac{50 \times 60 \times 325 \times 10^3}{58.5 \times V_1}$$

$$V_1 = \frac{50 \times 60 \times 325 \times 10^3}{58.5 \times 250} = 66666.67 \text{ liters}$$

Total volume of hard water softened = 66666.67 liters.

Practice problems

1. A zeolite softener was completely exhausted and was regenerated by passing 100 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of sample of water of hardness 500 ppm can be softened by this softener.
[Ans 20512.8 liters]
2. A zeolite softener was completely exhausted after softening 145,000 liters of hard water. To regenerate the zeolite softener 540 liters of NaCl solution containing 110 g/liter of NaCl is required. Calculate the hardness of one liter water sample in ppm.
[Ans 350.13 ppm]
3. 200 liters of NaCl solution containing 85 g/liter of NaCl was required to regenerate a completely exhausted zeolite softener. How many liters of hard water of hardness 600 ppm can be softened by the softener.
[Ans 24216.5 liters]
4. When a zeolite softener was completely exhausted it was regenerated by passing 200 liters of NaCl solution containing 120 g/liter of NaCl. How many liters of a sample of water of hardness 550 mg/liter can be softened by the zeolite softener before regenerating it again.
[Ans 37296.037 liters]

Ion Exchange Process – Deionisation or Demineralisation of Water

Ion exchange process is defined as the reversible exchange of ions in the structure of an ion exchanger to ions in solution that is brought in contact with it.

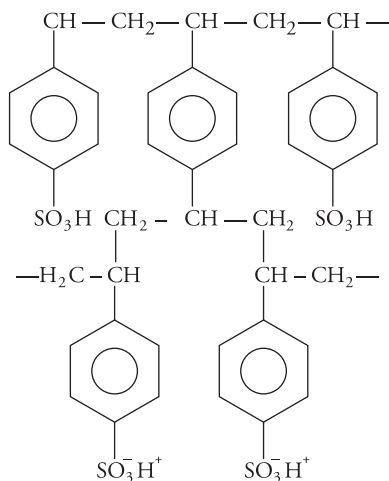
The resins used for the purpose are called ion exchange resins. They are porous, insoluble, cross linked, long chain organic polymers capable of exchanging ions.

Two types of resins are employed for the softening of water.

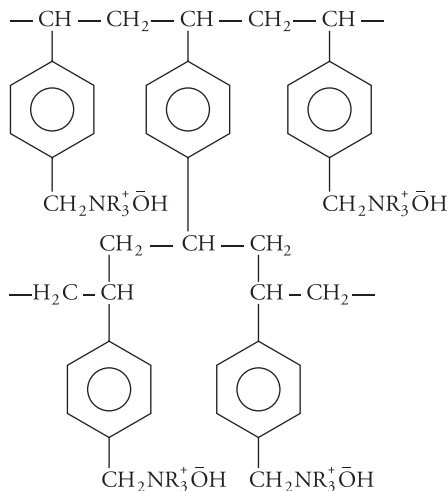
(i) *Cation exchange resin*

They are materials capable of exchanging a cation in their structure to the cation in solution. For softening of water, the resins used should be capable of exchanging H^+ ions in their structure to other cations in solution. Commonly used resins are styrene divinyl benzene copolymers, which on sulphonation or carboxylation become capable of exchanging hydrogen ions with the cations in water. They are represented as $R-H^+$ (R represents insoluble polymer matrix and H is the exchangeable ion).

Amberlite IR-120 and Dowex-50 are examples of commercially available cation exchange resins.

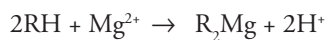
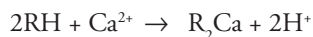
**Figure 2.6** Cation exchange resin(ii) **Anion exchange resin**

They are materials capable of exchanging an anion in their structure (for water softening the exchangeable anion should be OH^- ion) to anion in solution. Anion exchangers employed for water softening are styrene divinyl benzene or amine formaldehyde copolymers, which contain basic functional group such as amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These after treatment with dilute NaOH solution become capable of exchanging OH^- ions with the anions in water. They are represented as R^+OH^- (where R^+ is the insoluble polymer matrix and OH^- is the exchangeable ion). Amberlite 400 and Dowex-3 are examples of commercially available anion exchange resins. The structure of a typical anion exchange resin is given in Figure 2.7.

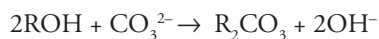
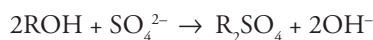
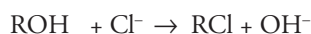
**Figure 2.7** Anion exchange resin

Process The hard water is first passed through a column containing cation exchange resin. All cations are removed and equivalent amount of H^+ ions are released from this column to water. The water coming out of this chamber has low pH.

The exchange reactions are



After this the water is passed into second column containing anion exchange resin. All the anions are removed and an equivalent amount of OH^- ions are released.



The H^+ ions released from cation exchange column and OH^- ions released from anion exchange column combine to produce water molecule.

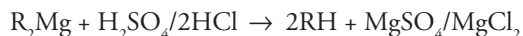
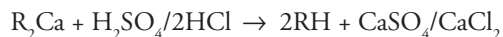


The water coming out of the exchanger is free from all cations (except H^+) and anions (other than OH^-). This ion free water is known as deionised water or demineralised water and has a neutral pH.

Regeneration

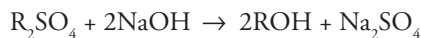
After sometime the resin loses all its H^+ and OH^- ions and then its capacity to exchange ions is lost. In such a condition they are said to be exhausted.

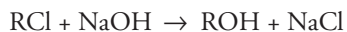
The exhausted cation exchange resin is regenerated by passing a solution of HCl or H_2SO_4 .



The column is then rinsed with distilled water to remove the salts formed. Ideally, HCl is used for regeneration as $CaCl_2$ and $MgCl_2$ are more soluble.

The anion exchange resin is regenerated by passing a dilute solution of NaOH and then washing with distilled water





NaCl , Na_2SO_4 are removed by washing with distilled water.

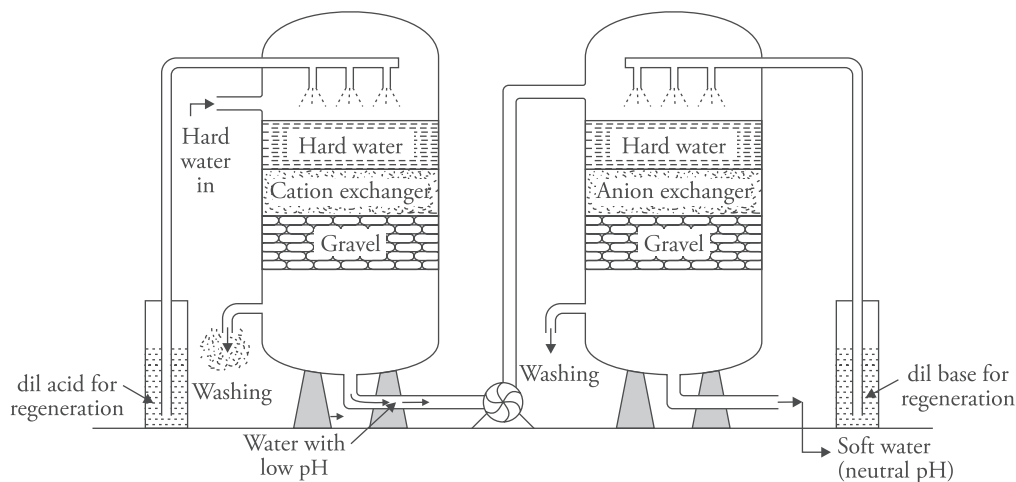


Figure 2.8 Ion exchange process

Advantages

1. The process can be used to soften highly acidic or alkaline water.
2. Unlike zeolite process the soft water does not contain sodium ions.
3. It removes all cations and anions other than H^+ and OH^- ions.
4. All ionisable impurities are removed.
5. It produces water of very low residual hardness (about 2 ppm).

Disadvantages

1. The process is expensive, both the equipment and resin are costly.
2. Turbid water decreases the efficiency of the process.

2.11 Municipal Water Supply

Water used for domestic purposes is consumed for various activities like drinking, cooking, bathing, washing, cleaning, etc. It is important that the water consumed for drinking and cooking should be free of impurities. Nearly 80% of the diseases are caused by contaminated water. The common requirements for potable water are

1. It should be clear, colorless, free from solids.
2. It should have good taste and should be odorless.
3. It should be soft.
4. It should be abundant and cheap.
5. Micro-organism and disease producing bacteria should not be present.
6. It should not have objectionable dissolved gases but sufficient dissolved oxygen should be present.
7. It should be free from harmful metallic salts.
8. Radioactive substance should not be present.
9. It should be free from fluorides, chlorides and phenolic compounds.
10. Corrosive metals should not exist.

Water treatment for domestic use employs the following steps:

1. Screening
2. Sedimentation
3. Filtration
4. Disinfection

(i) **Screening**

It is used to remove suspended impurities by passing water through screens having large number of holes when the floating materials are retained by them. Screens are vertical bars with perforations. Water is passed through them where the suspended and floating impurities are removed. To ensure complete removal of such impurities water is first passed through coarse screens and then through fine screens, which consist of woven wire, cloth or perforated plates mounted on a rotating disc or drum partially submerged in the flow. Fine screens should be cleaned mechanically on a continual basis. One of the problems associated with the screening process is the disposal of screenings. In modern water treatment plants, comminutors are installed. The comminutor grinds the coarse material to fine particles, which can be handled satisfactorily at a later stage.

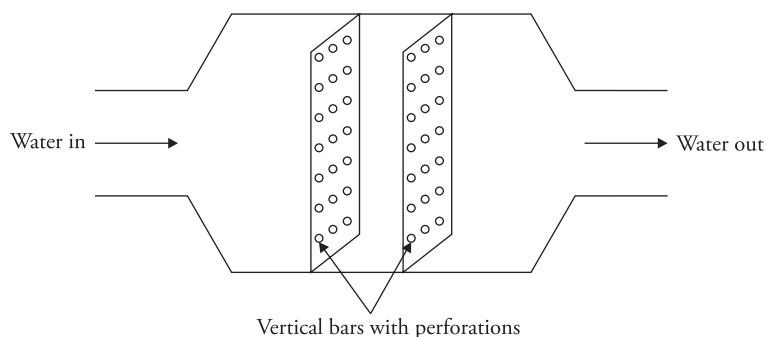


Figure 2.9 Screening

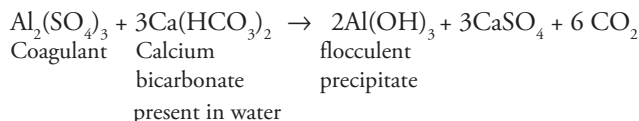
(ii) Sedimentation

It is the process of removing fine, suspended, colloidal impurities by allowing water to stand undisturbed in big tank about 5 m deep. Most of the suspended particles settle down at the bottom, due to the force of gravity. The clear supernant water is then drawn from the tank with the help of pumps. The retention period in a sedimentation tank ranges from 2–6 hours.

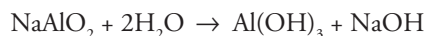
Fine suspended particles like mud particles and colloidal matter present in the water cannot settle by plain sedimentation. They are removed by sedimentation with coagulation.

Sedimentation with coagulation It is the process of removing fine suspended and colloidal impurities by addition of requisite amount of chemicals (coagulants) to water before sedimentation. Coagulant, when added to water, forms an insoluble gelatinous, flocculent precipitate, which traps very fine suspended impurities forming bigger flocs, which settle down.

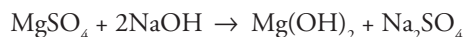
The coagulants mainly used are alum, ferrous sulphate or copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium aluminate, etc. They provide positive ions Fe^{3+} or Al^{3+} which neutralise the negative charge on the colloidal clay particles. After losing their charge the tiny particles come nearer to one another and combine to form bigger particles, which settle down, due to the force of gravity. The flocculants or coagulants are generally added in liquid form. Mixers are employed to ensure the proper mixing of the coagulants. General reactions during coagulation are



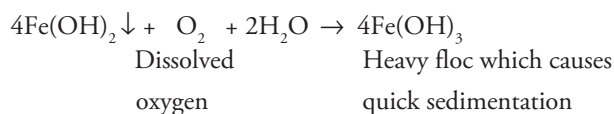
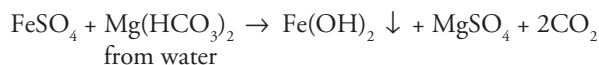
Alum reacts in the presence of alkalinity in water.



(This gives result in pH range 5.5-8.0. $\text{Al}(\text{OH})_3$ floc causes sedimentation whereas NaOH reacts with magnesium salts in water)



Similarly, FeSO_4 also reacts in slightly alkaline medium



(iii) Filtration

It is the process of separating colloidal and suspended impurities from water by passing it through a porous bed made of fine sand and other proper sized granular materials.

Filtration is carried out in a sand filter. It consists of a top thick layer of fine sand, placed over coarse sand layer followed by gravel. Water comes from the top. The suspended particles present in water that are of bigger size than the voids in the sand layer are retained there itself and the water becomes free of them. The sand layer may get choked after sometime and then it is to be replaced with clean sand for further action. This action is analogous to mechanical straining.

Small micro-organisms present in sand voids decompose organic matter and remove some of the biological impurities.

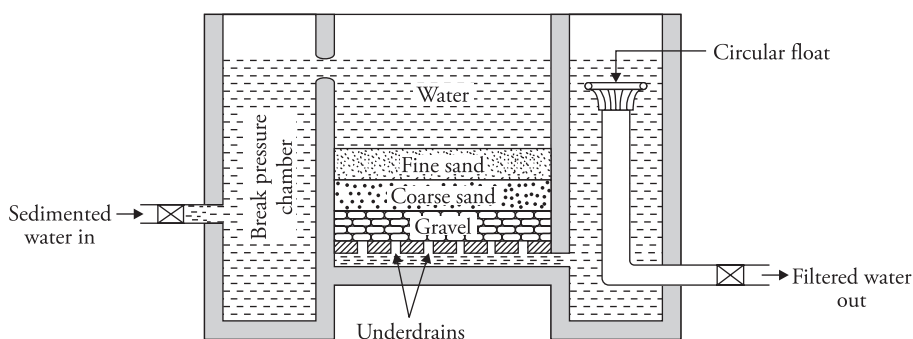


Figure 2.10 Sand filter

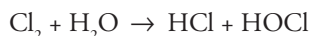
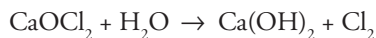
Advantages

Removes all suspended particles, colloidal impurities and organic matter.

(iv) Disinfection

It is the process of removing pathogenic bacteria, viruses and protozoa from water. A large number of methods are utilised, some of them are as follows:

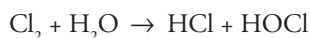
- (a) **Boiling** It is the simplest and easiest method to disinfect water. But it is useful only for small quantities of water. For proper disinfection, water should be boiled vigorously for 20–25 minutes.
- (b) **By adding bleaching powder** Bleaching powder (CaOCl_2) is a very good disinfectant. About 1 kg of bleaching powder per 100 kiloliters of water is mixed and water is allowed to stand undisturbed for several hours. The chemical action produces hypochlorous acid which is a powerful germicide and kills all the germs.



Germes + HOCl → Germes are killed

Drawbacks

- (1) Introduces calcium in water and hence increases its hardness.
 - (2) Bleaching powder deteriorates during storage.
 - (3) Excess CaOCl_2 gives bad taste and odor to treated water.
- (c) **Direct chlorination** Chlorine (either gaseous or in concentrated solution form) produces hypochlorous acid, which is a powerful germicide.



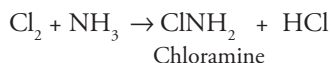
Germes + HOCl → Germes are killed

Advantage

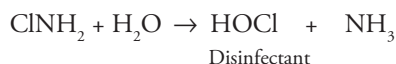
- (1) Economical, requires little space for storage.
- (2) Stable, does not deteriorate on storage.
- (3) Does not introduce calcium.

Disadvantages

- (1) Excess chlorine produces unpleasant taste and odor.
 - (2) Excess produces irritation on mucous membrane.
- (d) **By adding chloramines (ClNH_2):** Chloramine is formed by reacting chlorine and ammonia in the ratio 2:1



It is more lasting than chlorine alone, hence it is a better disinfectant



Advantages

- (1) Excess does not produce irritating odor.
- (2) It imparts good taste to treated water.

Break Point Chlorination (or free residual chlorination)

When chlorine is added to water and the sample of water is analysed for available chlorine it is found that the available chlorine is less than added. This is because the chlorine added in water is consumed not only for destroying the germs but also for oxidising the organic impurities, reducing substances and coloring matter in water.

If a graph is plotted between the amount of chlorine added and the free residual chlorine a plot as shown in Figure 2.11 is obtained. This graph has four stages:

Stage I: For lower doses of chlorine all the added chlorine is used in oxidising the reducing compounds in water hence there is no residual chlorine in water (part *ab* of the graph).

Stage II: On further addition of chlorine formation of chloro-organic compounds and chloramines takes place. Chloramines act as chlorine reserve and contribute in the chlorine test just as free chlorine does. Hence the graph shows an increase in residual chlorine to a maximum level shown by *bc* in the curve.

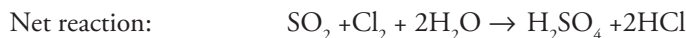
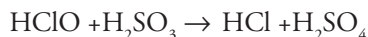
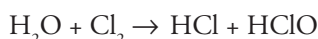
Stage III: On further addition of chlorine, the oxidation of chloramines and chloro-organic compounds takes place. The amount of residual chlorine decreases and reaches a minimum shown by point *d* in the graph. This point is termed as the break point. At this point water is completely free of all kinds of impurities and is of potable water quality. Addition of chlorine upto this point is termed as break point chlorination, which may be defined as the chlorination of water to such an extent that not only the pathogenic bacteria but also the organic matter, reducing impurities, coloring matter and odours from water is oxidised.

Stage IV: After the break point chlorine is not consumed further and the added chlorine is equal to the available chlorine and the graph once again shows an increase in the level of residual chlorine (part *de* in the graph.)

Advantages of break point chlorination:

- (1) It removes all compounds that impart colour, bad odour and unpleasant taste to water.
- (2) It destroys all organic matter, dissolved ammonia and microorganisms in water and prevents the growth of weeds in water.

Dechlorination: The excess chlorine added in water after break point imparts bad taste and colour to water and hence it has to be removed. It can be removed by passing water over activated charcoal or by the addition of SO_2 or by the use of Na_2SO_3



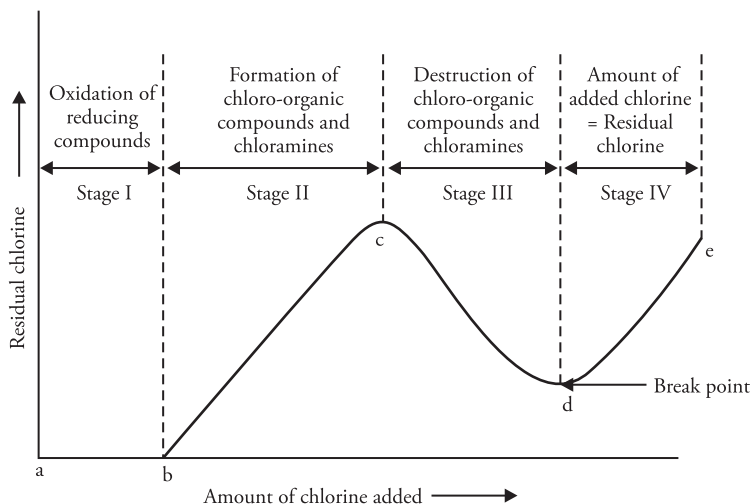
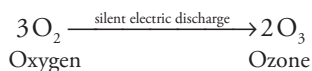


Figure 2.11 Graphical representation of break point chlorination

- (e) **Ozonisation** Ozone is produced by passing silent electric discharge through cold and dry oxygen



Ozone is highly unstable and breaks down liberating nascent oxygen



Nascent oxygen is a powerful oxidising agent and kills all the bacteria as well as oxidises the organic matter present in water. For disinfection by ozone, ozone is passed through water in a sterilising tank. The disinfected water is removed from the top. The contact period is about 10–15 minutes and dose is 2–3 ppm.

Advantages

- (1) Ozone sterilises, bleaches, decolorises and deodorises water.
- (2) Excess of ozone in water is not harmful as it decomposes to give oxygen.
- (3) There is no irritation of mucous membrane as is in the case of chlorine treatment.
- (4) Ozone improves the taste of water. Highly potable water is thus sterilised with ozone.

Disadvantages Ozonisation is a very expensive process. Moreover ozone is a corrosive agent. It corrodes stainless steel, cast iron, copper, rubber and ebonite.

- (f) **By adding KMnO_4** It is generally used to disinfect surface water systems containing bad taste and odor. When KMnO_4 is added to water, it gives purple color to water which finally disappears when the oxidation is completed. It removes H_2S , Fe and Mn. The normal dosage of KMnO_4 is about 1–2 mg/L within a period of 4–6 hours. It is generally used in rural areas where supplies are from wells.

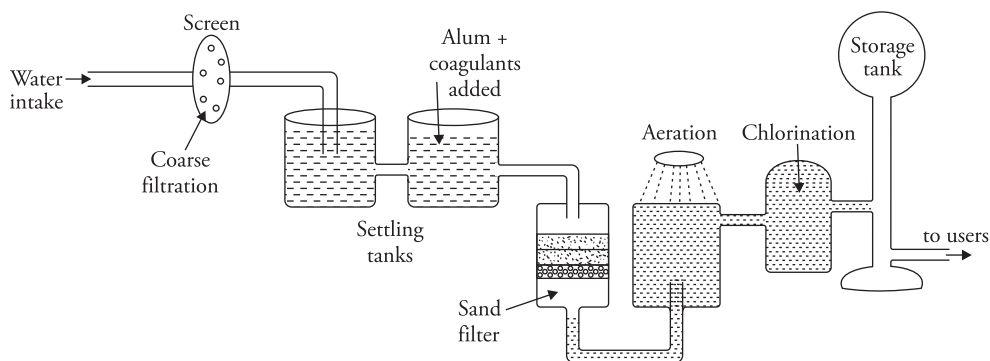


Figure 2.12 Schematic representation of a municipal water supply system

2.12 Desalination of Water

Water is a good solvent. It contains dissolved solids in it, depending upon the amount of dissolved solid water may be grouped as follows:

1. Fresh water (having < 1000 ppm of dissolved solids)
2. Brackish water (having > 1000 ppm but < 35000 ppm of dissolved solids)
3. Sea water (having > 35000 ppm of dissolved solids)

Thus water containing high concentration of salts in it is called brackish water. Due to the presence of large quantities of salts, it is salty in taste and is unfit for domestic and industrial purpose. This water can be put to good use by removing the salt content from it. *The process used for the removal of salts from water is called desalination.*

Various techniques employed for desalination are

1. Reverse osmosis
2. Electro dialysis
3. Ultra filtration
4. Flash evaporation

Reverse osmosis

Osmosis is defined as the process of spontaneous flow of solvent particles through a semi permeable membrane from a dilute solution to a concentrated solution (from lower concentration to higher concentration). The diffusion of solvent particles takes place on account of hydrostatic pressure called osmotic pressure, which drives solvent molecules in search of equilibrium.

If an external pressure equal to osmotic pressure is applied on the concentrated solution the process of osmosis will stop and if the external pressure exceeds osmotic pressure, solvent will be squeezed out of the concentrated solution. This process is called reverse osmosis.

Thus in reverse osmosis, pure water is separated from its contaminants rather than removing contaminants from water. This process is also known as super-filtration or hyper filtration. The semi permeable membranes are usually made up of cellulose acetate, polymethacrylate or polyamide polymers.

Advantages This process removes lead, calcium, magnesium, sodium, potassium, aluminium, chloride, nitrate, fluoride, sulphate, boron, most microorganisms and organic chemicals from water.

Disadvantages It requires large volume of water. *It may take as much as 90 liters water to recover 5 liters of useable water.*

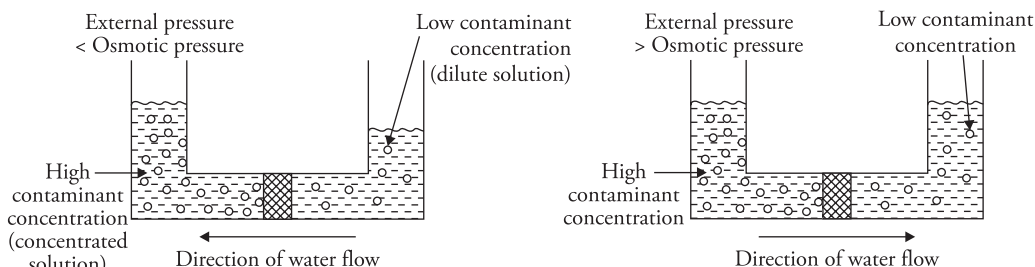


Figure 2.13 (a) Normal osmosis. (b) Reverse osmosis

Electrodialysis

It is a method in which the charged ions (salts) are removed from water by passing direct current, using electrodes and thin rigid ion selective semi permeable membranes.

Principle and working Consider a cell which is divided into three compartments using semi permeable membranes. Two electrodes (anode and cathode) are placed in the outer compartments and saline water is introduced in all the three compartments. When electric current is passed through saline water, the sodium ions (Na^+) move towards cathode (negative pole) and the chloride ions (Cl^-) move towards anode (positive pole) through the membrane.

Hence the concentration of brine decreases in the middle compartment and increases in the two side compartments. Desalinated (pure water) is obtained from the middle compartments, while the concentrated brine solution in side compartments is later replaced by fresh sea water.

A = Anion permeable membrane

C = Cation permeable membrane

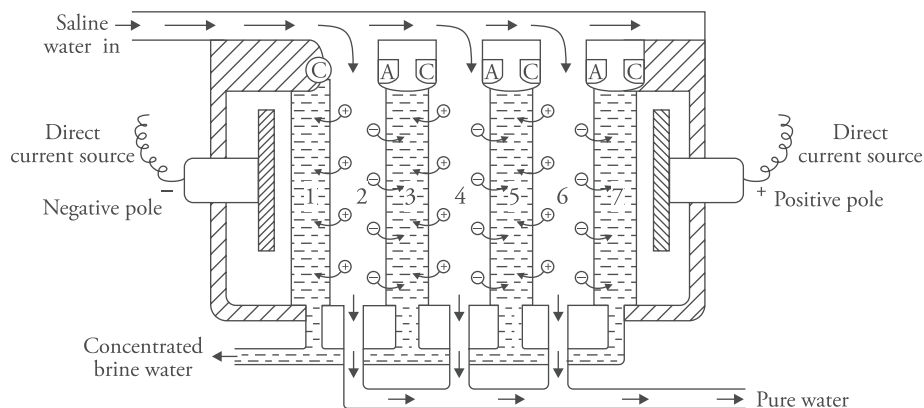


Figure 2.14 *Electrodialysis*

For more efficient separation ion selective membranes are employed. An ion selective membrane has permeability for one kind of ions only. For example, anion selective membrane allows the passage of anion and the cation selective membrane allows the passage of cations.

An electrodialysis cell consists of alternate cation and anion selective membranes. The cathode is placed near the cation selective/permeable membrane and the anode is placed near the anion selective membrane. Saline water is passed under a pressure of about $5\text{--}6\text{ kg m}^{-2}$ between membrane pairs and an electric field is applied perpendicular to the direction of water flow. Under the influence of the strong electric field the sodium ions (Na^+) start moving towards cathode through the membrane. As a result, there is depletion of ions in the even numbered compartments and the concentrations of ions in the odd numbered compartments increases. The desalinated water, free of ions is collected separately, whereas concentrated water of the odd numbered compartments is replaced from time to time by fresh lot of saline water.

Advantages

1. It is a compact unit and is cost effective and economical.
2. This technique is useful for the production of fresh water in arid-coastal regions.
3. The method is used when very high purification is not required.

Ultra filtration

Ultra filtration is the process of removing high molecular-weight substances like colloidal materials, organic and inorganic polymeric molecules like proteins by using semi permeable membranes with pore sizes in the range of 0.1 to 0.001 micrometer. Low molecular weight organic molecules and inorganic ions such as sodium, calcium, potassium and magnesium are not removed by this process.

The extent to which dissolved solids and microorganisms are removed is determined by the size of the pores in the membranes. Substances larger than the pore size are fully removed whereas those

smaller than the pore size cannot be removed. The size of the molecules retained by the membrane is defined by the molecular weight cut off (MWCO) of the membrane used.

The process of ultra filtration uses hollow fibers of membrane material. The feed water flows inside the hollow fibers. Suspended solids and solutes of high molecular weight are retained inside the hollow membrane (these retained particles are called retentate), while water and low molecular weight solutes pass through the membrane. These particles which pass through the membrane are called permeate.

The membranes commonly used for commercial ultra filtration are 'polysulfone' and cellulose acetate membranes.

Molecular weight cut off The retention properties of ultra filtration membranes are expressed by molecular weight cut-off (MWCO). This value refers to the approximate molecular weight of a dilute solute which is 90% retained by the membrane. For instance, a membrane that removes dissolved solids with molecular weight of 10,000 and higher has a MWCO of 10,000.

Factors affecting ultra filtration

The performance of an ultra filtration system depends on several factors:

- (i) **Flow across the membrane surface** Greater the flow velocity of the liquid across the membrane greater will be its permeate rate.
- (ii) **Pressure** The permeate rate will be directly proportional to the pressure applied across the membrane surface.
- (iii) **Temperature** The permeate rate is directly proportional to the temperature. It increases with the rise in temperature.

Applications

1. Ultra-filtration is used for the removal of suspended solids, colloids, cysts, bacteria and virus from water.
2. Purification of surface water, ground water to make them potable.
3. Removal of pathogens from milk.
4. Ultra filtration finds use in cheese manufacture.
5. It is used for desalting and solvent exchange of proteins.
6. It is used for the recovery of enzymes.
7. It is used in combination with reverse osmosis for pre-treatment of sea water in desalination plants.
8. Used in the treatment of waste water.
9. In medical field the process finds use in blood dialysis and other blood treatments.
10. It is also used in metal industry (oil/ water emulsion separation, paint treatment), filtration of effluents from paper pulp mill, in textile industry, dairy industry (milk, cheese) and food industry (proteins), etc.

Flash Evaporation

In this method sea water is heated to high temperature and then fed into a series of chambers. These chambers are maintained at reduced pressure. Because of sudden drop in pressure, the water gets evaporated very quickly. This is known as flash evaporation. The steam formed is condensed by the incoming sea water passing through coils as shown in Figure 2.15. The concentrated brine then passes to the second chamber which is at still lower pressure. Hence more water evaporates which is also condensed. In the similar manner water passes through a series of 4 to 40 chambers in order of increasingly reduced pressure. As a result more and more water is recovered which is collected and the concentrated brine solution is removed by blow-down process.

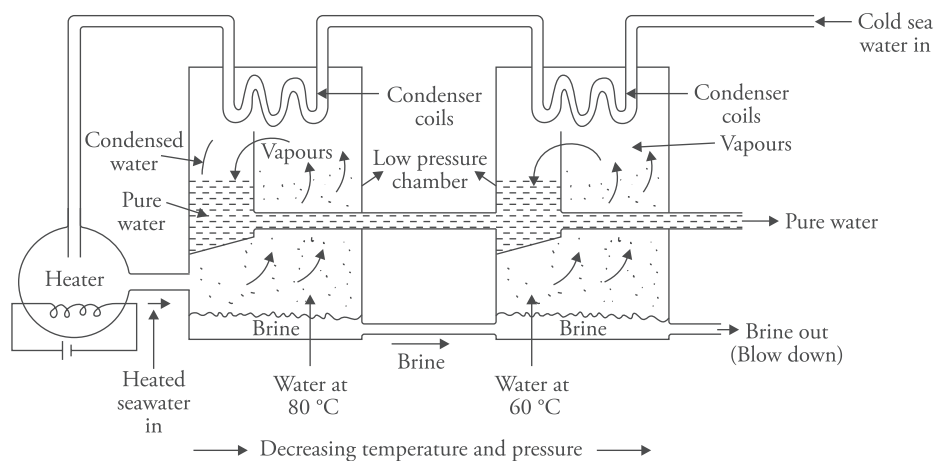


Figure 2.15 Flash evaporation

2.13 Defluoridation

Fluorine is an active element found in rocks. Weathering of fluoride bearing minerals from rocks, volcanoes increases the fluoride content in water particularly in ground water. The fluoride concentration in surface water seldom exceeds 0.3 ppm, but depending on the geomorphological conditions the fluoride content in ground water can exceed the acceptable limit of 1.0 ppm leading to chronic health problems in many parts of the country. Within permissible limits fluoride helps to protect teeth enamel and makes it more resistant but excess fluorine in water causes fluorosis which leads to weakening and bending of bones, decay of teeth, etc. Therefore it is mandatory to adopt measures to control fluoride content in potable water. If other options of drinking water are not available then defluoridation (removal of excess fluoride) of water should be adopted. The commonly used defluoridation techniques are as follows:

- Chemical precipitation (Nalgonda technique)
- Adsorption/ion exchange

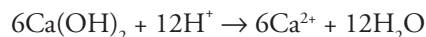
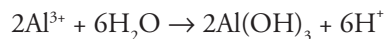
- Reverse osmosis
- Solar distillation

Fluoride can be removed from water by adsorption on bone charcoal, activated carbon, activated alumina, tamarind gel, etc. Ion exchange method and reverse osmosis have been discussed in the preceding sections. Solar distillation is distillation of water in the presence of sunlight. Here we shall discuss the chemical method to remove fluoride from water.

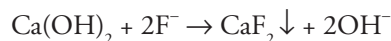
Nalgonda Technique:

This technique owes its name to the village Nalgonda in Telangana where it was pioneered. This method consists in the removal of fluoride from water by adding chemicals like alum and lime followed by flocculation, sedimentation and filtration. It was first developed by NEERI scientists in India and its first report was published in 1975.

The process involves five steps namely mixing, flocculation, sedimentation, filtration and disinfection. Calculated quantity of alum and lime are added to water and the water is thoroughly mixed so that the chemicals react with the fluoride in water and form suitable precipitates. The chemical reactions involved are as follows:



Besides this some fluoride is also precipitated with calcium



Flocs containing fluorides, turbidity, bacteria and other impurities are allowed to stand for sometime so that they settle down. Water standing above is decanted carefully and is filtered using sand filters (discussed earlier). The filtered water is collected and disinfected by further addition of bleaching powder and then distributed.

Limitations

Although the Nalgonda technique is being widely used in households and for community defluoridation process it has certain limitations which are as follows:

- The method fails if the fluorine content in water is very high.
- The quantity of alum and lime has to be carefully controlled for proper results.
- Large quantities of sludge is formed which should be disposed off carefully.

2.14 Waste Water Management

Domestic sewage is the waste water from kitchens, bathrooms, lavatories, dishwashers, washing machines and toilets. It generally does not include industrial or agricultural waste water.

Sewage treatment or domestic waste water treatment is the process of removing physical, chemical and biological contaminants from waste water with the objective of producing treated effluent and solid waste (sludge) for discharge or reuse back into the environment.

The main components of sewage treatment process are as follows:

- (1) collection, (2) conveyance, (3) treatment and (4) disposal
- (1) *Collection of waste water* The waste water from households is transferred to the drain pipes which are connected to the main drain. These pipes are made of either cement or plastic.
- (2) *Conveyance or transport of waste water* The domestic waste water from residential or commercial complexes enters the sewer lines laid in the main streets by the municipality. A manhole which is a cemented chamber covered with a cast iron lid is provided for regular inspection and cleaning of the sewer lines. The sewerage network so laid carries the entire sewage of the city to the sewerage treatment plant.
- (3) *Treatment of sewage* Sewage treatment include four steps:
 - (a) *Pretreatment or preliminary treatment* It involves the removal and size reduction of large objects like stones, twigs, leaves, rags, metals, plastics and other floating impurities. It involves five steps:
 - (i) Screening
 - (ii) Presedimentation
 - (iii) Microstraining
 - (iv) Preaeration
 - (v) Prechlorination
 - (b) *Primary treatment or physico-chemical treatment* It involves the removal of colloidal particles and other settleable impurities.
 - (c) *Secondary treatment or biological treatment* It is a biological process to convert organic matter in sewage into bacterial mass followed by removal of the products.
 - (d) *Tertiary treatment or advance treatment* Different advanced techniques are employed to remove various nutrients and for disinfecting water.
- (a) ***Pretreatment or preliminary treatment*** Preliminary treatment devices are designed to remove weeds, leaves, branches of trees, floating debris as well as gravel, sand, silt (called gritty substances), fats, oils, greases (called FOG), which if not removed can damage or clog the pumps and equipments used in sewage treatment. The steps involved in preliminary treatment process are as follows:
 - (i) *Screening* This step involves the removal of large objects by passing water through a series of perforated vertical bars called screens. To ensure complete removal of suspended and free floating impurities water is first passed through coarse screens and then through fine screens. A comminutor is employed to grind the screenings (solid impurities left behind) into small size particles that can be easily handled.

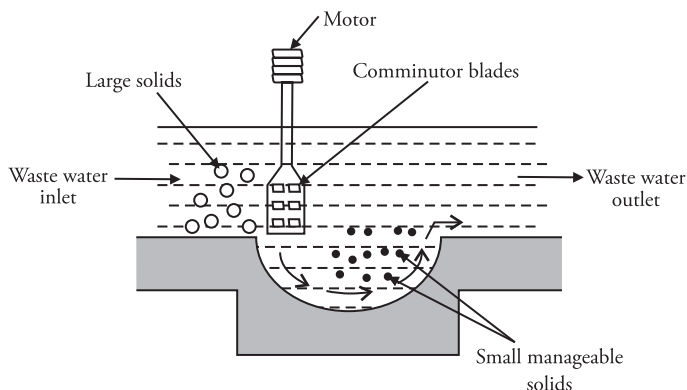


Figure 2.16 Comminutor

- (ii) **Presedimentation** It is used to remove gravel, sand and silt (grit) from raw water before it enters into the main treatment units, otherwise they can damage the pumps, equipments and other parts of the water treatment plant. Sand traps and cyclone degritter are employed to remove grit from water. In a sand trap the water passes at low velocity so that the gritty substances settle under gravity. In cyclone degritter the grit is removed by centrifugal action.
- (iii) **Microstraining** After presedimentation the water is passed through a microstrainer which is a free floating rotating drum consisting of fine stainless steel mesh. By this process small aquatic organisms like algae, fungi and diatoms are removed.
- (iv) **Pre-aeration** It is the aeration of waste water before primary treatment. It helps to reduce BOD, assist in the removal of grease and oil in waste water and to freshen up septic water prior to further treatment. For this, waste water is agitated with air in an aerator so that the lighter impurities float and are skimmed off.
- (v) **Prechlorination** It is the chlorination of waste water prior to primary treatment. Prechlorination does not disinfect water but prevents further decay of waste water. It is used to control odour, prevent decay of organic matter and reduce the biological oxygen demand of water.
- (b) **Primary treatment** It involves the removal of colloidal particles and other settleable impurities from the pretreated water. For this the pretreated water is kept in big tanks called primary clarifiers or primary sedimentation tanks where coagulants are added and the faecal solids and colloidal impurities are allowed to settle down. Detention time is typically 3 hours in tanks 10–15 feet deep. Particles too small to be settled out in this tank must be removed by filtration or other methods. Grease and oil rise to the surface and are skimmed off and the sedimented water is decanted.

Primary treatment is capable of removing 80–90% of total dissolved solids, 65% of suspended solids and upto 45% of BOD substances. After this stage a homogenous liquid is obtained which is capable of being treated biologically.

- (c) **Secondary or biological treatment:** The main objective of this step is to degrade the biological content of sewage derived from human waste, food waste and detergent. Secondary treatment is meant to remove soluble and colloidal organics which remain after primary treatment. It is conceptually similar to the process of decomposition taking place in nature. In this method, organic wastes are degraded microbially in the waste treatment plants. Presence of adequate microbial population and supply of oxygen is required for the effective operation of this process. Two commonly used processes are

- Trickling filter process
- Activated sludge process

Trickling filter process In this process the water to be treated is sprinkled over a bed of rocks covered with a layer of biological growth mass. The rock bed is nearly three meters in depth and is loosely packed to allow circulation of air. As water trickles over the bed the organic matter is consumed and degraded by the microbial growth. As the microorganisms consume the organic matter, the thickness of the slime film increases to a point where it can no longer be supported on the solid media and gets detached from the surface. This process is known as *sloughing*. This sloughed organic matter gets discharged into the effluent. A settling tank which follows the trickling filters removes the detached bacteria and also some suspended solids.

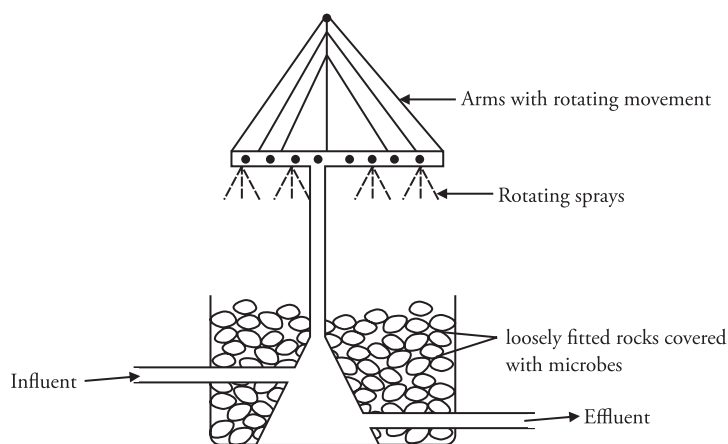


Figure 2.17 Trickling filter

Activated sludge process This process is more popular than the trickling filter process. In this method the soluble and unsettlable biodegradable organic compounds are degraded by bacteria in an aeration tank. Waste water after primary treatment enters an aeration tank where the organic matter is brought in contact with recycled sludge (from secondary clarifier), which is heavily laden with bacteria. Air necessary for the survival of bacteria is bubbled in the aeration tank. In the presence of oxygen, these microorganisms feed on the organic matter in waste water and convert it into stabilised low energy contents like sulphates and carbonates.

The microorganisms grow rapidly (because of availability of food/organic matter and air) and form an active mass of microbes and that is why the process is termed as the activated sludge process. This effluent from aeration tank containing the flocculent microbes flows into a settling tank called the secondary clarifier where the sludge settles at the bottom. This sludge containing microbes is called activated sludge or biological floc. It is removed and disposed off after treatment and a small portion is recycled in the aeration tank to act as the seed for the further growth of microbes.

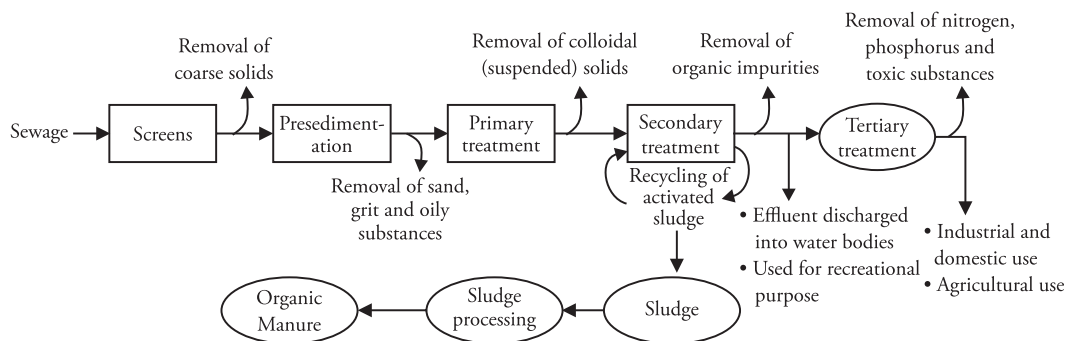


Figure 2.18 Schematic representation of Sewage/Domestic waste water treatment

- (d) **Tertiary treatment or advanced treatment** The primary and secondary treatment is sufficient to meet the waste water effluent standards. If water of very high purity is required then advanced waste water treatment is carried out. The main function of tertiary treatment is to remove the load of nitrogen and phosphorus compounds from the effluents. It also aims at removing toxic substances from water and disinfecting water. It is achieved in a number of ways:

Phosphorus removal It is removed by precipitation. The effluent after secondary treatment is mixed with calcium oxide which reacts with phosphorus compounds in waste water forming calcium phosphate which is removed and used as a fertilizer.

Phosphorus can also be removed by adding polyphosphate accumulating bacteria which feed on phosphorus containing compounds. Later this biomass enriched with phosphorus is separated and used as biofertiliser.

Nitrogen removal A nitrification – denitrification process is used for the removal of nitrogen from waste water. In the first step nitrogen is converted into nitrates with the help of microorganisms and then these nitrates are released into the atmosphere by converting them into nitrogen using denitrifying bacteria.

Toxic substances are removed by special techniques

After this the water is disinfected. (Disinfection of water has been discussed earlier in the preceding sections.)

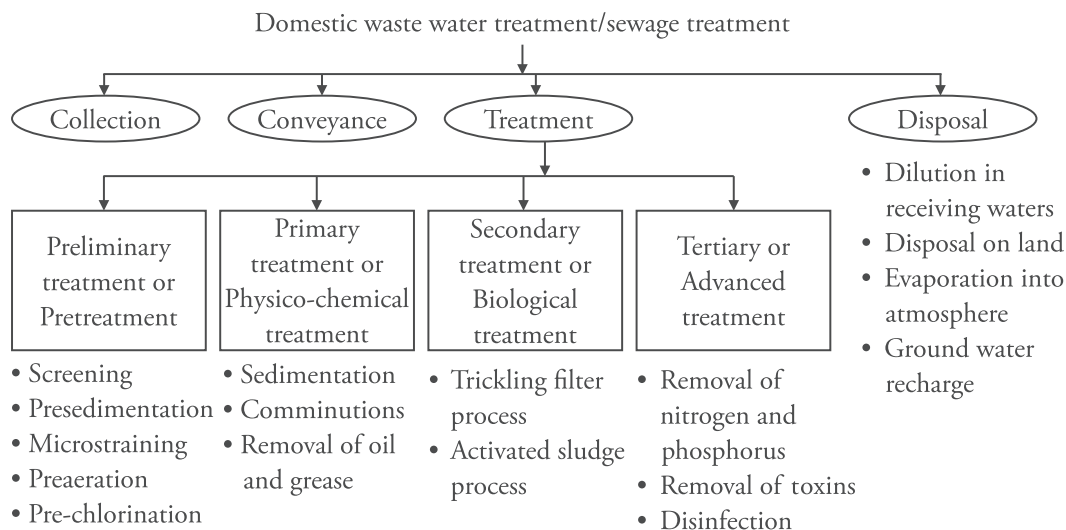


Figure 2.19 Summary of the Domestic waste water/Sewage treatment process

2.15 Chemical Analysis of Water

Determination of Hardness

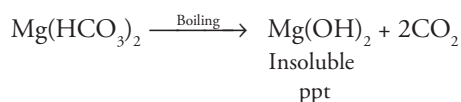
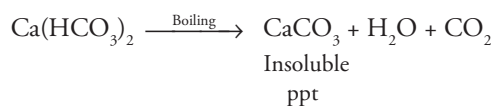
Hardness of water can be determined by the following methods:

1. O. Hehner's method
2. EDTA method
3. Soap titration method

The EDTA method is the most accurate and widely used method for the estimation of hardness in water.

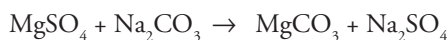
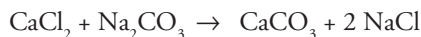
Determination of hardness by O.Hehner's method

- (a) Temporary hardness in a water sample is caused by $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$. It is removed on boiling



The temporary hardness of the water sample can be determined by titrating the water sample with standard HCl solution before and after boiling.

- (b) Permanent hardness caused by chlorides, sulphates and nitrates of calcium and magnesium cannot be removed by boiling. They can however be removed by boiling the water sample with a known excess of standard sodium carbonate. The chloride and sulphates form insoluble carbonates. The residual sodium carbonate is determined by titration with standard HCl solution. The amount of soda used is equivalent to the permanent hardness.



Procedure

- (A) **Determination of temporary hardness** Pipette out 50 mL of the water sample in a conical flask, add 2-3 drops of methyl orange indicator and titrate against N/50 HCl solution. At the end point the color changes to pink and say V_1 mL of HCl is consumed at the end point.

After this take fresh 250 mL of the sample water in 500 mL flask. Gently boil it for half an hour, cool the solution and filter it. Wash the precipitate with distilled water and collect all the washings and filtrate. Now titrate 50 mL of this solution with standard HCl solution using methyl orange as an indicator. Let the volume of HCl consumed be V_2 mL.

Calculation

Volume of N/50 HCl consumed by temporary hardness present in 50 mL of water sample

$$= (V_1 - V_2) \text{ mL}$$

$$\begin{array}{ccc} N_1 V_1 & = & N_2 V_2 \\ \text{Water} & & \text{HCl} \\ \text{sample} & & \end{array}$$

$$N_1 \times 50 = N/50 \times (V_1 - V_2)$$

$$N_1 = (V_1 - V_2)/(50 \times 50)$$

Hardness in terms of equivalent of CaCO_3

$$= \text{Normality of water} \times \text{equivalent weight of } \text{CaCO}_3$$

$$= \frac{(V_1 - V_2)}{50 \times 50} \times 50 \text{ g/L}$$

$$= \frac{(V_1 - V_2)}{50 \times 50} \times 50 \times 1000 \text{ mg/L}$$

$$\text{Temporary hardness} = 20(V_1 - V_2) \text{ ppm}$$

- (B) **Determination of permanent hardness** Take 250 mL of hard water sample in a conical flask and boil for half an hour to remove temporary hardness. Filter and add 50 mL of N/50 Na_2CO_3 solution. Boil for another 25–30 minutes. All chlorides and sulphates are converted into carbonates. Filter the solution and wash the precipitate several times with hot distilled water, collecting all the washings in the conical flask. Now titrate 50 mL of this solution against standard HCl solution using methyl orange as an indicator.

Let the titre value be V mL

\therefore Volume of N/50 Na_2CO_3 solution used for removing permanent hardness in 50 mL water sample = (50 – V) mL

$$\begin{matrix} N_3 & V_3 & = & N_4 & V_4 \\ \text{Water} & & & \text{HCl} & \\ \text{sample} & & & & \end{matrix}$$

$$N_3 \times 50 = N/50 \times (50 - V)$$

$$N_3 = \frac{(50 - V)}{50 \times 50}$$

Hardness in terms of equivalent of CaCO_3

= Normality of water \times equivalent weight of CaCO_3

$$= \frac{(50 - V)}{50 \times 50} \times 50 \text{ g/L} = \frac{(50 - V)}{50 \times 50} \times 50 \times 1000 \text{ mg/L}$$

Permanent hardness = 20 (50 – V) ppm.

Solved Examples

- Calculate the temporary hardness when the following observations were recorded

Observations

Before boiling

Volume of water sample for each titration = 50 mL

Volume of N/50 HCl consumed = 14 mL

After boiling

Volume for each titration = 50 mL

Volume of N/50 HCl consumed = 10 mL.

Solution

Volume of HCl consumed by the temporary hardness present in water = 14 – 10 = 4 mL

Hardness of the water sample $N_1 V_1 = N_2 V_2$

N_1 = Normality of hardness in water sample; V_1 = volume of water

N_2 = Normality of HCl, V_2 = Volume of HCl consumed

$$N_1 \times 50 = \frac{N}{50} \times 4$$

$$N_1 = \frac{4}{50 \times 50}$$

Temporary hardness in terms of CaCO_3 equivalent in ppm = Normality of water sample \times Equivalent weight of $\text{CaCO}_3 \times 1000$

$$= \frac{4}{50 \times 50} \times 50 \times 1000$$

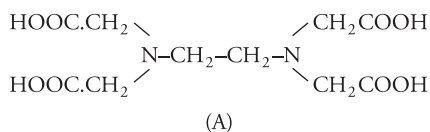
$$= 80 \text{ ppm}$$

Practice Problems

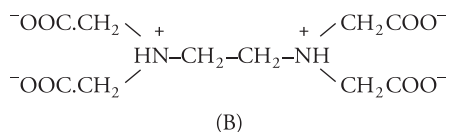
- 100 mL of tap water was titrated with N/50 HCl with methyl orange as an indicator. If 28 mL HCl were required, calculate the hardness as parts of CaCO_3 per 10,000 parts of water. The hardness is temporary. [Ans 2800 parts per 10000 parts of water]
- In an experiment to determine the hardness of a sample of water, 25 mL of N/50 Na_2CO_3 solution was added to 100 mL of water sample. After completion of precipitation of the insoluble carbonates the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution when 10 mL of the acid was required. Calculate the degree of hardness and comment on the nature of hardness so determined. [Ans permanent hardness 150 ppm]

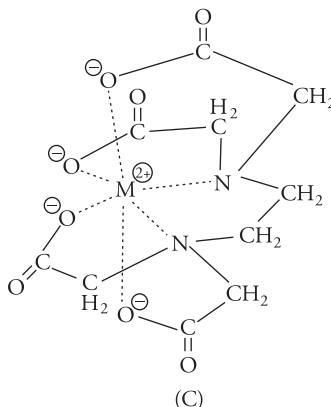
Estimation of hardness by EDTA Method

This is a complexometric titration as ethylene diamine tetra-acetic acid (EDTA) forms a stable complex with Ca^{2+} and Mg^{2+} ions in the pH range 8–10.



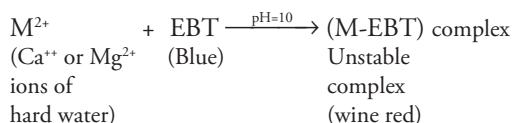
Its anion is





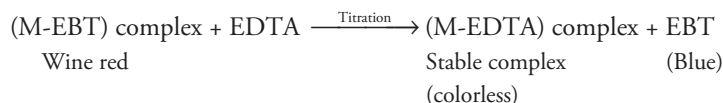
- (A) Structure of EDTA
 (B) Structure of dianion of EDTA, H_2Y^{2-}
 (C) Structure of an M^{2+} -EDTA chelate MY^{2-}

In order to determine hardness, hard water is buffered to a pH value of 10 using NH_4OH-NH_4Cl buffer and a few drops of Eriochrome black-T indicator (EBT) are added. EBT forms a weak unstable wine red complex with metal ions.



where M = Ca and Mg ions.

During the course of titration of water sample against EDTA, EDTA combines with free Ca^{2+} or Mg^{2+} ions to give very stable metal-EDTA complex which is colorless.



Thus at equivalent point, there is a change in color from wine red (due to M-EBT) to blue (due to free EBT).

The various steps involved in this method are as follows:

- Preparation of standard hard water** Dissolve 1.0 g of pure, dry $CaCO_3$ in minimum quantity of dilute HCl and evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 liter solution. Each mL of this solution contains 1mg of $CaCO_3$ equivalent hardness.
- Preparation of EDTA solution**
0.01 M EDTA is prepared by dissolving 3.7 g of its disodium salt (molar mass = 372.28) in distilled water and making it up to 1 liter.
- Preparation of indicator** Dissolve 0.5 g of Eriochrome black – T in 100 mL of alcohol

4. **Preparation of buffer solutions** Add 67.5 g of NH_4Cl to 570 mL of concentrated ammonia solution and then dilute with distilled water to 1 liter.

Procedure

1. **Standardisation of EDTA solution** Fill the burette with EDTA solution after washing and rinsing. Pipette out 50 mL of standard hard water in a conical flask (1 mL of standard hard water = 1 mg of CaCO_3 equivalent hardness). Add 10 mL of buffer solution and 2–3 drops of indicator (EBT). Titrate with EDTA solution, till wine red color changes to clear blue. Let the volume of EDTA consumed be V_1 mL.
2. **Determination of total hardness of water** Titrate 50 mL of unknown hard water by the same procedure as done above, let the volume of EDTA consumed this time be V_2 mL.
3. **Determination of permanent hardness of water** Take 250 mL of water sample in a 500 mL beaker and boil it till the volume reduces to about 50 mL. Boiling causes all the bicarbonates to decompose to CaCO_3 and Mg(OH)_2 . Filter and quantitatively collect the filtrate and washings in a 250 mL conical flask and make the volume to 250 mL with distilled water. Titrate 50 mL of this water sample against EDTA as done in step (1). Let the volume of EDTA used be V_3 mL.

CALCULATIONS

Step 1 Standardisation of EDTA solution

V_1 mL of EDTA = 50 mL of standard hard water

(Since each mL of standard hard water contains 1 mg of CaCO_3 equivalent hardness)

Therefore, V_1 mL of EDTA = 50 mg of CaCO_3 equivalent hardness

or 1 mL of EDTA = $50/V_1$ mg of CaCO_3 (1)

Step 2 Determination of total hardness

50 mL of unknown hard water = V_2 mL of EDTA

(Since 1 mL of EDTA has $50/V_1$ mg of CaCO_3 hardness – from Eq. (1))

$$= V_2 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness} \quad (2)$$

The hardness given by Eq. (2) is the hardness in 50 mL water sample \therefore hardness in 1000 mL water sample

$$\begin{aligned} &= V_2 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 \\ &= 1000 \times \frac{V_2}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness} \end{aligned}$$

Hence total hardness of water = $1000 \times \frac{V_2}{V_1}$ mg/L or ppm

Step 3 Determination of permanent hardness of water

As 50 mL of boiled water = V_3 mL of EDTA

Again as 1 mL EDTA = $\frac{50}{V_1}$ mg of CaCO_3 equivalent hardness [from Eq. (1)]

$\therefore V_3$ mL of EDTA = $V_3 \times \frac{50}{V_1}$ mg of CaCO_3 equivalent hardness (3)

hardness as given by Eq. (3) is the hardness in 50 mL boiled water

\therefore hardness in 1000 mL of boiled water = $V_3 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 = 1000 \times \frac{V_3}{V_1}$ mg/L

Hence permanent hardness of water = $1000 \times \frac{V_3}{V_1}$ mg/L or ppm

Temporary hardness = Total hardness – Permanent hardness

$$= 1000 \times \frac{V_2}{V_1} - 1000 \times \frac{V_3}{V_1}$$

$$\text{or temporary hardness} = \frac{1000 (V_2 - V_3)}{V_1} \text{ ppm}$$

Volume of EDTA can be equated with CaCO_3 equivalent as follows

1000 mL of 1 M EDTA = 100 g of CaCO_3

1000 mL of 0.01 M EDTA = 1 g of CaCO_3

1 mL of 0.01 M EDTA = 1 mg of CaCO_3

1 mL of 0.02 N EDTA = 1 mg of CaCO_3

Solved Examples

- 250 mL of a water sample on EDTA titration with Eriochrome Black –T consumed 13 mL of 0.022 N EDTA till end point is reached. Calculate the hardness of water ?

Solution

1 mL of 0.01 M EDTA = 1 mg of CaCO_3 equivalents

$$13 \text{ mL of } 0.022 \text{ M EDTA} = \frac{1 \times 13 \times 0.022}{1 \times 0.01} = 28.6 \text{ mg of } \text{CaCO}_3$$

This amount of hardness is present in 250 mL of water sample.

$$\text{Hardness present in 1 liter} = \frac{28.6}{250} \times 1000 = 114.4 \text{ ppm}$$

2. 100 mL of a sample of water required 15 mL of 0.01 M EDTA for titration using Eriochrome Black –T as indicator. In another experiment, 100 mL of the same sample was boiled to remove the temporary hardness, the precipitate was removed and the cold solution required 8 mL of 0.01 M EDTA using Eriochrome Black –T as indicator. Calculate the total hardness, permanent hardness and temporary hardness in mg/L of CaCO_3 equivalent.

Solution

As we know 1 mL of 0.01 M EDTA = 1 mg of CaCO_3 eq. hardness. (1)

Determination of total hardness of water

100 mL of water sample = 15 mL of 0.01 M EDTA = 15 mg of CaCO_3 eq. hardness.
[From Eq. (1)]

$$\therefore 1000 \text{ mL of water sample} = \frac{15}{100} \times 1000 = 150 \text{ mg/L}$$

Total Hardness = 150 mg/L

Determination of permanent hardness of water

100 mL of boiled hard water = 8 mL of 0.01 M EDTA = 8 mg of CaCO_3 eq. hardness

$$\therefore 1000 \text{ mL of water sample} = \frac{8}{100} \times 1000 = 80 \text{ mg/L}$$

Temporary Hardness = Total Hardness – Permanent Hardness

$$= 150 - 80 = 70 \text{ mg/L}$$

3. 0.28 g of CaCO_3 was dissolved in HCl and the solution was made to one liter with distilled water. A total of 100 mL of the above solution required 28 mL of EDTA solution on titration.

100 mL of the hard water sample required 35 mL of the same EDTA solution on titration. After boiling 100 mL of this water, cooling, filtering and then titration required 10 mL of EDTA solution. Calculate the temporary and permanent hardness of water.

Solution

Step (i) *Standardisation of EDTA solution*

Given, 1 liter of standard hard water contains 0.28 g CaCO_3

or, 1000 mL of standard hard water contains 280 mg CaCO_3

or, 1 mL of standard hard water contains 0.28 mg CaCO_3 (i)

According to the question

28 mL of EDTA solution \equiv 100 mL of standard hard water

According to eq (i) 1 mL of standard hard water has 0.28 mg of CaCO_3

\therefore 100 mL of standard hard water has 100×0.28 mg of CaCO_3

or, 28 mL EDTA solution = $100 \times 0.28 = 28$ mg of CaCO_3

1 mL EDTA solution = $\frac{28}{28} = 1$ mg of CaCO_3

Step (ii) *Determination of total hardness of water*

Given, 100 mL of unknown hard water sample \equiv 35 mL of EDTA $\equiv 35 \times 1$

= 35 mg of CaCO_3 equivalent hardness

\therefore 1000 mL (or 1 liter) of unknown hard water sample = $\frac{35}{100} \times 1000$

= 350 mg of CaCO_3 equivalent hardness

Hence **Total Hardness = 350 ppm**

Step (iii) *Determination of permanent hardness of water*

Given, 100 mL of boiled water \equiv 10 mL of EDTA $\equiv 10 \times 1 = 10$ mg of CaCO_3 eq. hardness.

\therefore 1000 mL (or 1 liter) of unknown boiled water = $\frac{10}{100} \times 1000 = 100$ mg of CaCO_3 eq. hardness.

Permanent Hardness = 100 ppm

Step (iv) *Determination of temporary hardness of water*

Temporary Hardness = Total Hardness – Permanent Hardness

$$350 - 100 = 250 \text{ ppm}$$

Temporary Hardness = 250 ppm

4. 25 mL of standard hard water consumes 12 mL of standard EDTA solution. 25 mL of hard water sample consumes 8 mL of EDTA solution. After boiling the sample, 25 mL of the boiled and cooled hard water consumes 6 mL of standard EDTA solution. Calculate the total, permanent and temporary hardness.

Solution

It is assumed that 1 mL of standard hard water has 1 mg of CaCO_3 equivalent hardness.

Step (i) *Standardisation of EDTA*

25 mL of standard hard water = 12 mL of EDTA = 25 mg of CaCO_3 eq. hardness.

$$1 \text{ mL of EDTA} = \frac{25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness.} \quad (1)$$

Step (ii) *Total hardness*

$$25 \text{ mL of hard water sample} = 8 \text{ mL of EDTA} = 8 \times \frac{25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness.} \quad [\text{From Eq. (1)}]$$

$$1000 \text{ mL of hard water sample} = 8 \times \frac{25}{12} \times \frac{1000}{25} = 666.67 \text{ ppm}$$

Hence **Total Hardness = 666.67 ppm**

Step (iii) *Determination of permanent hardness of water*

$$\text{Given, 25 mL of boiled water} = 6 \text{ mL of EDTA} = \frac{6 \times 25}{12} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1000 \text{ mL (or 1 liter) of unknown boiled water} = \frac{6 \times 25 \times 1000}{12 \times 25} = 500 \text{ ppm.}$$

Permanent Hardness = 500 ppm

Step (iv) *Determination of temporary hardness of water:*

Temporary Hardness = Total Hardness – Permanent Hardness

$$666.67 - 500 = 166.67 \text{ ppm}$$

Temporary Hardness = 166.67 ppm

5. Calculate the hardness of water sample whose 10 mL required 20 mL of EDTA. 20 mL of CaCl_2 solution whose strength is equivalent to 1.5 g of CaCO_3 per liter required 30 mL of EDTA solution.

Solution

1 liter of standard hard water = 1.5 g = 1500 mg of CaCO_3

or 1 mL of standard hard water = 1.5 mg of CaCO_3 (1)

Step (i) *Standardisation of EDTA*

20 mL of standard hard water = 30 mL of EDTA

30 mL of EDTA = 20×1.5 mg of CaCO_3 equivalent hardness [From Eq (1)]

1 mL of EDTA = $\frac{20 \times 1.5}{30}$ mg of CaCO_3 equivalent hardness. (2)

Step (ii) *Total hardness*

10 mL of sample hard water = 20 mL of EDTA

= $\frac{20 \times 20 \times 1.5}{30}$ mg of CaCO_3 equivalent hardness [From Eq. (2)]

1000 mL of sample hard water = $\frac{20 \times 20 \times 1.5}{30} \times \frac{1000}{10} = 2000$ ppm

Total hardness = 2000 ppm

Practice Problems

1. A standard hard water contains 15 g of CaCO_3 per liter. 20 mL of this water sample required 25 mL of EDTA solution, 100 mL of sample water required 18 mL of EDTA solution. The sample after boiling required 12 mL EDTA solution. Calculate total, permanent and temporary hardness of the given water sample in ppm.

[Ans Total hardness = 2160 ppm; Permanent hardness = 1440 ppm;
Temporary hardness = 720 ppm]

2. The EDTA was used to find out permanent and temporary types of hardness in a given hard water sample. Following observations were recorded:
- (i) 22 mL of EDTA was consumed by 50 mL of standard hard water (containing 1 mg of CaCO_3 per mL).
 - (ii) 50 mL water sample consumed 27 mL EDTA solution.

(iii) 50 mL water sample after boiling, filtering consumed 20 mL of EDTA solution.

[Ans Total hardness = 1227.27 ppm; permanent hardness = 909 ppm;
temporary hardness = 318.2 ppm]

3. 1.0 g of CaCO_3 was dissolved in hydrochloric acid and made upto 1000 mL. 50 mL of this solution required 46 mL of EDTA solution for titration. 50 mL of hard water sample required 20 mL of the same EDTA solution. After boiling the sample of hard water, 50 mL of it consumed 12 mL of EDTA solution. Calculate the carbonate and non-carbonate hardness of the water sample.

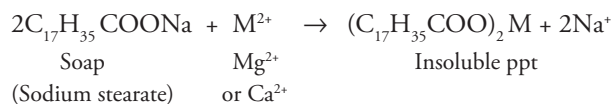
[Ans Total hardness = 434.78 ppm; permanent hardness (non-carbonate hardness) = 260.86 ppm; temporary hardness (carbonate hardness) = 173.92 ppm]

4. 0.25 g of CaCO_3 was dissolved in HCl and diluted to 250 mL. 100 mL of this solution required 20 mL of EDTA solution for titration. 100 mL of a hard water sample required 30 mL of the same EDTA solution for titration. 100 mL of the sample water on boiling, cooling and filtering required 10 mL of EDTA. Calculate the total, permanent and temporary hardness of the water sample.

[Ans Total hardness = 1500 ppm; permanent hardness = 500 ppm;
temporary hardness = 1000 ppm]

Soap titration method or Clarkes's Method

It is based on the principle that when soap solution is added to hard water, the hardness causing ions (Ca^{2+} , Mg^{2+} and other heavy metal ions) react with it forming insoluble precipitate of calcium and magnesium. Formation of insoluble precipitate continues till all the hardness causing ions have precipitated. After this the soap gives lather.



Also, the addition of soap solution to water decreases its surface tension. Even in distilled water, formation of lather takes place only after the lower critical value of surface tension is reached. The volume of soap solution required to form lather with distilled water (of zero hardness) is known as lather factor.

This volume (corresponding to lather factor) is to be subtracted from all titre values. Both total and permanent hardness in a given water sample can be estimated by this method. Temporary hardness can be calculated by subtracting the two.

Procedure

- (1) **Preparation of standard hard water** Dissolve 1.0 g of pure, dry CaCO_3 in minimum quantity of dilute HCl. Boil to dryness to expel excess of acid and CO_2 . Dissolve the residue in distilled water to make 1 liter solution. The hardness of this solution is 1 g/liter or 1000 ppm or 1 mg/mL.
- (2) **Preparation of soap solution** Dissolve 100 g of pure dry caustic soap in 800 mL of alcohol plus 200 mL of distilled water.

- (3) **Standardisation of soap solution** The burette is rinsed and filled with soap solution. In a 250 mL glass-stoppered bottle, 50 mL of standard hard water is taken (the hardness of standard hard water is 1 mg/mL). Soap solution is added 0.2 mL at a time. After each addition, the contents of stoppered bottle are vigorously shaken until lather formation starts. Now, soap solution is added at the rate of 0.1 mL at a time till lather formed after vigorous shaking persist for 2 minutes. Let the volume of soap solution used be V_1 mL.
- (4) **Lather factor of distilled water** 50 mL of soap solution is titrated against distilled water, till lather persists for two minutes. Let the volume used be V mL. This volume is to be subtracted from all titre values.
- (5) **Determination of total hardness of water** The above procedure is repeated, taking 50 mL of water sample. Let the titre value of soap be V_2 mL.
- (6) **Determination of permanent hardness of water** 250 mL of water sample is taken in a beaker. It is boiled and the volume is reduced to 50 mL (boiling causes all bicarbonates to decompose into insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$). The precipitate is filtered and washed with distilled water. The filtrate and washings are collected in a 250 mL conical flask. The volume is then made to 250 mL by adding distilled water. 50 mL of this water sample is then taken and titrated against soap solution by the procedure as done above. Let the titre value of soap solution be V_3 mL.

Calculation

- (i) *Standardisation of soap solution*

50 mL of standard hard water = $(V_1 - V)$ mL of soap solution

As standard hard water has 1 g/liter or 1 mg/mL CaCO_3 so 50 mL standard hard water contains $50 \times 1 = 50$ mg of CaCO_3

Thus $V_1 - V$ mL of soap solution = 50 mg of CaCO_3 equivalent hardness

$$\text{or 1 mL of soap solution} = \frac{50}{V_1 - V} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness} \quad (1)$$

- (ii) *Determination of total hardness of water*

50 mL of hard water = $(V_2 - V)$ mL of soap solution

$$\therefore 1 \text{ mL of soap solution has } \frac{50}{V_1 - V} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness from Eq. (1)}$$

Hence $(V_2 - V)$ mL of soap solution has

$$= (V_2 - V) \times \frac{50}{V_1 - V} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness (2)}$$

$$\text{Hardness in 1000 mL of hard water} = (V_2 - V) \times \frac{50}{V_1 - V} \times \frac{1000}{50}$$

$$\text{Total hardness} = 1000 \times \frac{V_2 - V}{V_1 - V} \text{ ppm}$$

(iii) *Determination of permanent hardness in water*

50 mL of boiled water = $V_3 - V$ mL of soap solution

$$= (V_3 - V) \times \frac{50}{V_1 - V} \text{ mg of CaCO}_3 \text{ equivalent hardness} \quad [\text{from Eq. (1)}]$$

$$\text{Hardness in 1000 mL of boiled water} = (V_3 - V) \times \frac{50}{V_1 - V} \times \frac{1000}{50}$$

$$= 1000 \times \frac{V_3 - V}{V_1 - V} \text{ mg/L of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Permanent hardness} = 1000 \times \frac{V_3 - V}{V_1 - V} \text{ ppm}$$

(iv) *Determination of temporary hardness*

Temporary hardness = Total hardness – Permanent hardness

$$= 1000 \times \frac{V_2 - V}{V_1 - V} - 1000 \times \frac{V_3 - V}{V_1 - V} \text{ ppm}$$

$$= \frac{1000}{V_1 - V} [(V_2 - V) - (V_3 - V)]$$

$$= \frac{1000}{V_1 - V} (V_2 - V_3) \text{ ppm}$$

$$\text{Temporary hardness} = \frac{1000}{V_1 - V} (V_2 - V_3) \text{ ppm}$$

Solved Examples

- Estimate different types of hardness present in hard water sample from the following data obtained in soap titration method, when 100 mL of water is titrated with soap solution:
 - Standard hard water (400 mg/L of CaCO_3) = 36.6 mL of soap solution.
 - Total hardness = 18.6 mL of soap solution.
 - Permanent hardness = 6.2 mL of soap solution.
 - Lather factor = 0.6 mL of soap solution.

Solution

Step (i) *Standardisation of soap solution*

Given, 1 liter of standard hard water (SHW) = 400 mg of CaCO_3 equivalent hardness

\therefore 100 mL of SHW = 40 mg of CaCO_3 equivalent hardness

Volume of soap solution required to precipitate 100 mL of hard water = $36.6 - 0.6 = 36.0$ mL

36.0 mL of soap solution = 40 mg of CaCO_3 equivalent hardness.

$$1 \text{ mL of soap solution} = \frac{40}{36} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness} \quad (1)$$

Step (ii) *Determination of total hardness of water*

100 mL of hard water = $18.6 - 0.6 = 18$ mL soap solution.

100 mL of hard water = $18 \times \frac{40}{36} = 20$ mg of CaCO_3 equivalent hardness

\therefore 1 liter of hard water = $\frac{20}{100} \times 1000 = 200$ mg/L

Thus, **total hardness = 200 ppm**

Step (iii) *Determination of permanent hardness of water*

100 mL of boiled water = $6.2 - 0.6 = 5.6$ mL of soap solution

100 mL of boiled water = $5.6 \times \frac{40}{36} = 6.22$ mg of CaCO_3 equivalent hardness

\therefore 1 liter of boiled water = $\frac{6.22}{100} \times 1000 = 62.2$ mg/L

Permanent hardness = 62.2 ppm

Step (iv) *Determination of temporary hardness*

Temporary hardness = Total hardness – Permanent hardness

$200 - 62.2 = 137.8$ mg/L = 137.8 ppm

Temporary hardness = 137.8 ppm

Practice problems

1. A standard hard water was prepared by dissolving 0.2 g of pure and dried CaCO_3 in one liter of distilled water. The soap solution was consumed for each titration against 50 mL of the water sample. The following observations were obtained
 - (i) Volume with standard hard water = 20.5 mL.
 - (ii) Volume with hard water sample = 9.0 mL.
 - (iii) Volume for permanent hardness = 3.0 mL.
 - (iv) Lather factor = 1.0 mL.

Find out each type of hardness in ppm.

[Ans Total hardness = 82 ppm; permanent hardness = 20.5 ppm;
temporary hardness = 61.5 ppm]

2. A standard hard water solution was prepared by 250 mg of CaCO_3 in 1000 mL of distilled water. And 17.2 mL of soap solution was consumed, when titrated with 50 mL of standard hard water. Lather factor for 50 mL of distilled water is 0.6 mL. The 50 mL of given sample of hard water consumed 7.6 mL of soap solution. 6.8 mL of soap solution was consumed when titrated with 50 mL of boiled filtered hard water sample. Find out total, permanent and temporary hardness.

[Ans Total hardness = 105.42 ppm; permanent hardness = 93.373 ppm;
temporary hardness = 12.047 ppm]

Alkalinity

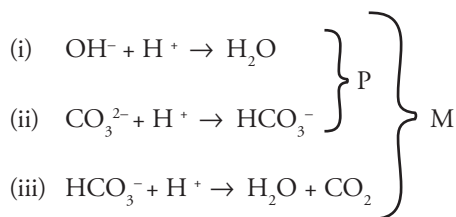
Alkalinity of water is a measure of total content of those substances which increase the hydroxide ions concentration (OH^-) upon dissociation or due to hydrolysis.

Alkalinity of water is attributed to the presence of

- (i) Caustic alkalinity (due to OH^- and CO_3^{2-} ions) and
- (ii) Temporary hardness (due to HCO_3^- ions)

These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicator.

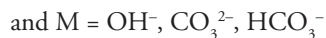
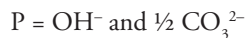
The determination is based on the following reactions



The titration of the water sample against a standard acid up to phenolphthalein end point (P) marks the completion of reaction (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one half of the normal carbonate present.

On the other hand, titration of the water sample against a standard acid to methyl orange end point (M) marks the completion of reaction (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions)

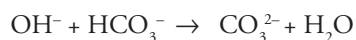
Thus,



Alkalinity in water may be due to the presence of the following combinations:

- (i) OH^- only
- (ii) CO_3^{2-} only
- (iii) HCO_3^- only
- (iv) OH^- and CO_3^{2-} together
- (v) CO_3^{2-} and HCO_3^- together

The possibility of OH^- and HCO_3^- together is ruled out, because of the fact that they combine instantaneously to form CO_3^{2-} ions



Thus, OH^- and HCO_3^- ions cannot exist together in water

On similar analogy, OH^- , CO_3^{2-} and HCO_3^- ions also cannot exist together.

Procedure Pipette out 100 mL of the water sample in a clean titration flask. Add 2–3 drops of phenolphthalein indicator. Run in N/50 H_2SO_4 (from a burette), till the pink color is just discharged. This is the first end point. Let the volume of acid used until phenolphthalein end point = V_1 mL. Then to the same solution, add 2 to 3 drops of methyl orange. Continue titration, till the pink color reappears. This is the second end point. Let *extra volume* of acid used to methyl orange end point = V_2 mL.

Calculations

100 mL of water up to phenolphthalein end point = V_1 mL of N/50 H_2SO_4

$$\therefore \underset{\text{Water}}{100 \text{ mL}} \times \underset{\text{Acid}}{N_p} = \underset{\text{Acid}}{V_1 \text{ mL}} \times \text{N/50}$$

$$N_p = \frac{V_1 \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{V_1}{5000} N$$

∴ Strength of alkalinity up to phenolphthalein end point in terms of CaCO_3 equivalent –
Strength = Normality \times Eq. weight of CaCO_3

$$= \frac{V_1}{5000} \times 50 \text{ g/L}$$

$$= \frac{V_1}{5000} \times 50 \times 1000 \text{ mg/L}$$

$$\mathbf{P = 10 V_1 \text{ ppm}}$$

Now 100 mL of water up to methyl orange end point

$$= (V_1 + V_2) \text{ mL of } N/50 \text{ H}_2\text{SO}_4$$

$$\therefore 100 N_m = (V_1 + V_2) \text{ mL} \times N/50$$

$$\text{or Normality } N_m = \frac{(V_1 + V_2) \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{(V_1 + V_2)}{5000} N$$

∴ Strength of total alkalinity in terms of CaCO_3 equivalent

$$= \frac{(V_1 + V_2)}{5000} \times 50 \text{ g/L} = \frac{(V_1 + V_2)}{5000} \times 50 \times 1000 \text{ mg/L}$$

$$\mathbf{M = 10(V_1 + V_2) \text{ ppm}}$$

- (i) When $P = 0$ both OH^- and CO_3^{2-} are absent and alkalinity in that case is due to HCO_3^- alone.
- (ii) When $P = M$ neither CO_3^{2-} nor HCO_3^- ions are present, only OH^- ions are present, Thus alkalinity due to $\text{OH}^- = P = M$.
- (iii) When $P = 1/2 M$ or $V_1 = V_2$ only CO_3^{2-} is present, since half of carbonate neutralisation (ie $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$) takes place with phenolphthalein, while complete carbonate neutralisation ($\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$; $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$) occurs when methyl orange indicator is used. Thus alkalinity due to $\text{CO}_3^{2-} = 2P$.
- (iv) When $P > 1/2 M$ or $V_1 > V_2$. In this case, besides CO_3^{2-} , OH^- ions are also present. Now half of CO_3^{2-} (i.e., $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$) is equal to $(M - P)$, so alkalinity due to complete $\text{CO}_3^{2-} = 2(M - P)$ and alkalinity due to $\text{OH}^- = M - 2(M - P) = (2P - M)$.
- (v) When $P < 1/2 M$ or $V_1 < V_2$, in this case, besides CO_3^{2-} , HCO_3^- ions are also present, now alkalinity due to $\text{CO}_3^{2-} = 2P$ and alkalinity due to $\text{HCO}_3^- = (M - 2P)$.

[Note If alkalinity is to be expressed in terms of individual components, then their chemical equivalent should be used instead of 50(for CaCO_3)]

Table 2.10 Calculation of alkalinity of water

S.No	Result of titration	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
1	$P=0$	Nil	Nil	M
2	$P=M$	P or M	Nil	Nil
3	$P=1/2M$ or $V_1 = V_2$	Nil	2P	Nil
4	$P>1/2M$ or $V_1 > V_2$	$2P-M$	$2(M-P)$	Nil
5	$P<1/2M$ or $V_1 < V_2$	Nil	2P	$M-2P$

Solved Examples

- 50 mL of a sample of water required 5 mL of $N/50 \text{ H}_2\text{SO}_4$ using methyl orange as indicator but did not give any coloration with phenolphthalein. What type of alkalinity is present? Express the same in ppm.

Solution

As the water sample does not give any coloration with phenolphthalein ($P = 0$), hence only HCO_3^- ions are present.

Now, 50 mL of water sample upto methyl orange end point = 5 mL of $N/50 \text{ H}_2\text{SO}_4$

$$\therefore 50 \text{ mL} \times N_M = 5 \text{ mL} \times N/50$$

$$\text{or Normality} = 5 \text{ mL} \times N/50 \times 1/50 = \frac{1}{500} \text{ N}$$

Strength of alkalinity in terms of CaCO_3 equivalents

$$= N_M \times \text{Equivalent Weight of } \text{CaCO}_3 = \frac{1}{500} \times 50 \text{ g/L} = \frac{1}{500} \times 50 \times 1000 \text{ mg/L} = 100 \text{ mg/L}$$

Alkalinity due to HCO_3^- ions = 100 ppm.

- 200 mL of water sample on titration with $N/50 \text{ H}_2\text{SO}_4$ using phenolphthalein as indicator gave the end point when 10 mL of acid were run down. Another lot of 200 mL of the sample also required 10 mL of the acid to obtain methyl orange end point. What type of alkalinity is present in the sample and what is its magnitude?

Solution

200 mL of water upto phenolphthalein end point \equiv 10 mL of $N/50 \text{ H}_2\text{SO}_4$

$$\therefore 200 \times N_p = 10 \times N/50$$

$$N_p = \frac{10}{200} \times \frac{N}{50}$$

Strength of phenolphthalein alkalinity in terms of CaCO_3 equivalents

Strength = $N_p \times \text{Equivalent Weight of } \text{CaCO}_3$

$$\text{Strength} = \frac{10}{200} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{10}{200} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 50 \text{ mg/L}$$

$$P = 50 \text{ ppm}$$

Similarly, $M = 50 \text{ ppm}$

Since $P=M$, hence only OH^- ions are present which are causing alkalinity. Hence, alkalinity due to $\text{OH}^- = 50 \text{ ppm}$.

3. 500 mL of a water sample on titration with $N/50 \text{ H}_2\text{SO}_4$ gave a titre value of 29 mL to phenolphthalein end point and another 500 mL sample on titration with same acid gave a titre value of 58 mL to methyl orange end point. Calculate the alkalinity of the water sample in terms of CaCO_3 and comment on the type of alkalinity present.

Solution

500 mL of water upto phenolphthalein end point $\equiv 29 \text{ mL of } N/50 \text{ H}_2\text{SO}_4$

$$\therefore 500 \times N_p = 29 \times N/50$$

$$N_p = \frac{29}{50 \times 500}$$

Strength of phenolphthalein alkalinity in terms of CaCO_3 equivalents

Strength = $N_p \times \text{Equivalent Weight of } \text{CaCO}_3$

$$\text{Strength} = \frac{29}{500} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{29}{500} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 58 \text{ mg/L}$$

$$P = 58 \text{ ppm}$$

Given 500 mL of water upto methyl orange end point $\equiv 58 \text{ mL of } N/50 \text{ H}_2\text{SO}_4$

$$\therefore 500 \times N_M = 58 \times N/50$$

$$N_M = \frac{58}{500} \times \frac{N}{50}$$

Strength = $N_M \times \text{Equivalent Weight of } \text{CaCO}_3$

$$\text{Strength} = \frac{58}{500} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{58}{500} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 116 \text{ mg/L}$$

$$M = 116 \text{ ppm}$$

Since $P = \frac{1}{2} M$, only CO_3^{2-} alkalinity is present in the water sample.

Hence,

Alkalinity in the water sample due to $\text{CO}_3^{2-} = 2P = M = 116 \text{ ppm}$

4. A sample of water was alkaline to both phenolphthalein and methyl orange. 100 mL of this water sample required 30 mL of N/50 H_2SO_4 for phenolphthalein end point and another 20 mL for complete neutralisation. Determine the type and extent of alkalinity present.

Solution

100 mL of water upto phenolphthalein end point \equiv 30 mL of N/50 H_2SO_4

$$\therefore 100 \times N_p = 30 \times N/50$$

$$N_p = \frac{30}{100} \times \frac{N}{50}$$

Strength of alkalinity upto phenolphthalein end point in terms of CaCO_3

Strength = $N_p \times$ Equivalent weight of CaCO_3

$$\text{Strength} = \frac{30}{100} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{30}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 300 \text{ mg/L}$$

P = 300 ppm

Given 100 mL of water upto methyl orange end point \equiv 30+20 = 50 mL of N/50 H_2SO_4

$$\therefore 100 \times N_M = 50 \times N/50$$

$$N_M = \frac{50}{100} \times \frac{1}{50}$$

Strength = $N_M \times$ Equivalent Weight of CaCO_3

$$\text{Strength} = \frac{50}{100} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{50}{100} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 500 \text{ mg/L}$$

M = 500 ppm

Since $P > \frac{1}{2} M$ therefore both OH^- and CO_3^{2-} are present.

Alkalinity due to $\text{OH}^- = 2P - M = 2 \times 300 - 500 = 100 \text{ ppm}$

Alkalinity due to $\text{CO}_3^{2-} = 2(M - P) = 2(500 - 300) = 400 \text{ ppm}$

\therefore the water sample contains

OH⁻ alkalinity = 100 ppm

CO₃²⁻ alkalinity = 400 ppm

5. A water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of a this water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and titration is further continued, the yellow color of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.

Solution

200 mL of water upto phenolphthalein end point \equiv 9.4 mL of N/50 HCl

$$\therefore 200 \times N_p = 9.4 \times N/50$$

$$N_p = \frac{9.4}{200} \times \frac{N}{50}$$

Strength of alkalinity upto phenolphthalein end point in terms of CaCO_3

Strength = $N_p \times$ Equivalent Weight of CaCO_3

$$\text{Strength} = \frac{9.4}{200} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{9.4}{200} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 47 \text{ mg/L}$$

P = 47 ppm.

As 200 mL of water upto methyl orange end point \equiv 9.4 + 21 = 30.4 mL of N/50 HCl

$$\therefore 200 \times N_M = 30.4 \times N/50$$

$$N_M = \frac{30.4}{200} \times \frac{1}{50}$$

Strength = $N_M \times$ Equivalent Weight of CaCO_3

$$\text{Strength} = \frac{30.4}{200} \times \frac{1}{50} \times 50 \text{ g/L} = \frac{30.4}{200} \times \frac{1}{50} \times 50 \times 1000 \text{ mg/L} = 152 \text{ mg/L}$$

M = 152 ppm

Since $P < \frac{1}{2} M$, hence CO_3^{2-} and HCO_3^- are present.

Alkalinity due to $\text{CO}_3^{2-} = 2P = 2 \times 47 = 94 \text{ ppm}$

Alkalinity due to $\text{HCO}_3^- = M - 2P = 152 - 94 = 58 \text{ ppm}$

\therefore the water sample contains

HCO_3^- alkalinity = 58 ppm

CO_3^{2-} alkalinity = 94 ppm

Practice problems

1. A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 mL of this water sample required 7.5 mL of N/50 HCl for neutralisation to phenolphthalein end point (P). At this stage a few drops of methyl orange were added. The acid required further was 14.5 mL of N/50 HCl for neutralisation to methyl orange end point (M). Calculate alkalinity of water as CaCO_3 due to the presence of carbonate and bicarbonate.

[Ans Alkalinity due to $\text{CO}_3^{2-} = 150 \text{ ppm}$

Alkalinity due to $\text{HCO}_3^- = 70 \text{ ppm}$]

2. 100 mL of a raw water sample on titration with N/50 H_2SO_4 required 12.4 mL of the acid to phenolphthalein end point and 15.2 mL of the acid to methyl orange end point. Determine the type and extent of alkalinity present in the water sample.

[Ans Alkalinity due to $\text{OH}^- = 96 \text{ ppm}$

Alkalinity due to $\text{CO}_3^{2-} = 56 \text{ ppm}$]

3. 100 mL of a raw water sample required 25 mL of N/50 H_2SO_4 for neutralisation to phenolphthalein end point. After this methyl orange indicator was added to it and further acid required was 3.0 mL. Calculate the alkalinity of water as CaCO_3 in parts per million.

[Ans Alkalinity due to $\text{OH}^- = 220 \text{ ppm}$

Alkalinity due to $\text{CO}_3^{2-} = 60 \text{ ppm}$; Total alkalinity = 280 ppm]

4. A water sample was alkaline to both phenolphthalein and methyl orange. 50 mL of the water sample required 18 mL of 0.02 N H_2SO_4 for phenolphthalein end point and another 6 mL for complete neutralisation. Describe the type and amount of alkalinity present.

[Ans Alkalinity due to $\text{OH}^- = 240 \text{ ppm}$

Alkalinity due to $\text{CO}_3^{2-} = 240 \text{ ppm}$; Total alkalinity = 480 ppm]

Estimation of Free Chlorine

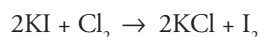
Chlorine is widely used for the disinfection of water. Chlorination is generally done with the help of bleaching powder or chlorine gas or with chloramines.

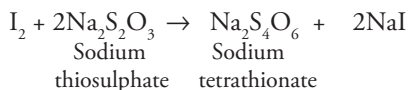
Excess of free chlorine present in water, makes the water unfit for drinking purposes as it not only imparts unpleasant taste to water but also adversely affects human metabolism. Hence the amount of free chlorine is estimated in municipal water before supplying it for domestic use.

Principle The estimation of free chlorine is based on the oxidation of KI by free chlorine i.e by iodometric titration.

Thus when water sample containing free chlorine is treated with potassium iodide solution, the free chlorine present in water oxidises potassium iodide and liberates an equivalent amount of iodine.

The liberated iodine is titrated against hypo solution ($\text{Na}_2\text{S}_2\text{O}_3$) using starch as indicator.





The end point is the disappearance of the blue color.

Procedure A known volume of sample water is pipetted out in a titration flask (say 50 mL). 10 mL of KI solution is added to it. The flask is then kept in dark for 5 minutes so that all the I_2 is liberated. The solution is then titrated against N/50 sodium thiosulphate solution using starch as the indicator. At the end point the color changes from deep blue to colorless. Let the volume of hypo used for titration be V mL. Then

$$\begin{array}{ccc} \text{Water} & & \text{Hypo} \\ \text{sample} & & \\ N_1 V_1 & = & N_2 V_2 \end{array}$$

$$N_1 \times 50 = N/50 \times V$$

$$\text{Normality of free chlorine} = \frac{N}{50 \times 50} \times V$$

$$\text{Strength of free chlorine} = \text{Normality of free chlorine} \times \text{equivalent weight of chlorine}$$

$$= \frac{V}{2500} \times 35.5 \text{ g/L}$$

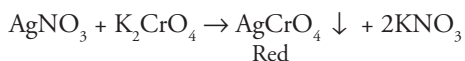
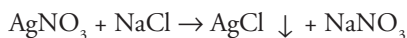
$$= \frac{V}{2500} \times 35.5 \times 1000 \text{ mg/L} = 14.2 V \text{ ppm}$$

Dissolved Chlorides

Chlorides are generally present in water as NaCl, MgCl_2 and CaCl_2 . Concentration of chlorides above 250 ppm imparts a bad taste to water making it unfit for drinking purposes.

Principle Chloride ions can be determined by titrating the water sample against standard solution of AgNO_3 using potassium dichromate as indicator (Argentometric titration)

When AgNO_3 is added to the water sample in the presence of K_2CrO_4 , the chlorides present in it are precipitated as AgCl. After the precipitation of all chloride ions, the extra drop of AgNO_3 gives a red precipitate of silver chromate. This marks the end point.



Procedure 50 mL of water sample is taken in a conical flask. 3-4 drops of freshly prepared K_2CrO_4 is added. The solution is titrated against N/50 $AgNO_3$ solution. Appearance of brick red color indicates the end point.

Let the volume of $AgNO_3$ used be V mL

$$\begin{array}{ll} \text{Water} & AgNO_3 \\ \text{Sample} & \text{solution} \\ N_1 V_1 & = N_2 V_2 \end{array}$$

$$N_{\text{chloride}} \times 50 = \frac{N}{50} \times V$$

$$N_{\text{chloride}} = \frac{V}{50 \times 50}$$

$$\text{Strength of chloride ions} = \frac{V}{2500} \times 35.5 \text{ g/L}$$

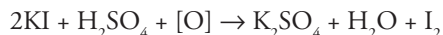
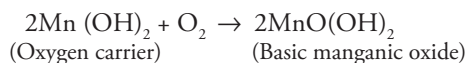
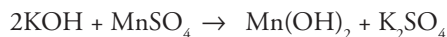
$$= \frac{V}{2500} \times 35.5 \times 1000 \text{ mg/L}$$

$$= 14.2 V \text{ ppm}$$

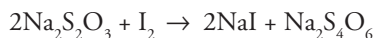
Dissolved oxygen

Oxygen dissolved in water is required by living organisms to carry out their biological processes. Dissolved oxygen is determined by the Winkler's method or iodometric titration.

Principle It is based on the fact that oxygen dissolved in water oxidises potassium iodide and an equivalent amount of iodine is liberated. The liberated iodine is titrated against standard hypo solution using starch as indicator. However since oxygen is in molecular state in water it is not capable of reacting with KI, so an oxygen carrier such as manganese hydroxide is used. $Mn(OH)_2$ is produced by the action of manganous sulphate ($MnSO_4$) with KOH.

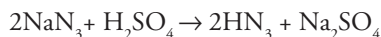


The iodine liberated in equivalent amount is titrated against hypo solution



Sometimes water contains substances like nitrates and sulphites which also react with KI to liberate iodine; hence the presence of these ions gives wrong results. Therefore it is important to eliminate these ions.

Sodium azide (NaN_3) is added to decompose the nitrate or sulphate present in water.



Reagents

- (i) **Manganous sulphate solution** 400 g of MnSO_4 is dissolved in 1 L of distilled water.
- (ii) **Alkaline azide solution** 150 g KI + 500 g NaOH and 20 g of NaN_3 in one liter of distilled water.
- (iii) **Sodium thiosulphate solution (N/100)** 2.48 g of $\text{Na}_2\text{S}_2\text{O}_3$ in 1 L of distilled water.

Procedure A known amount of water sample (250 mL) is taken in a stoppered bottle avoiding contact with air. 2 mL of MnSO_4 is added with the help of a pipette, dipping the end well below the water surface. Similarly 2.0 mL of alkaline azide solution is also added. The bottle is stoppered and shaken thoroughly. The brown precipitate so formed is dissolved in minimum quantity of concentrated H_2SO_4 . The bottle is shaken well to dissolve the precipitate. 100 mL of this solution is then titrated against hypo solution using freshly prepared starch as an indicator. The disappearance of blue color marks the end point. Let the volume of hypo solution used be V mL.

Calculation

O_2 in water Hypo

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = \frac{1}{100} \times V$$

$$N_1 = \frac{1}{100 \times 100} \times V$$

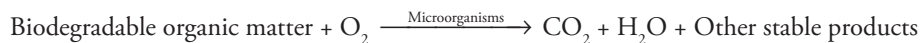
Strength of O_2 in water = Normality of $\text{O}_2 \times$ equivalent weight of O_2

$$= \frac{1}{10,000} \times 8 \text{ g/L}$$

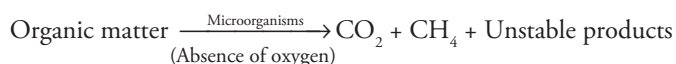
$$= \frac{1}{10,000} \times 8 \times 1000 \text{ mg/L} = 0.8 \times V \text{ ppm}$$

BIOLOGICAL OXYGEN DEMAND (BOD)

BOD measures the extent of pollution of waste water, sewage and industrial effluents. The waste water or polluted water generally contains organic matter. This organic matter may either be biodegradable or non biodegradable. The microorganisms feed on the biodegradable matter in the presence of oxygen (aerobically) to form stable, non objectionable end products.



However, if enough oxygen is not available, anaerobic oxidation (in absence of oxygen) takes place and harmful end products like H_2S , NH_3 and CH_4 are formed.



The amount of oxygen required by microorganisms to oxidise organic matter aerobically is called Biological Oxygen Demand (BOD). If the BOD of the sample is high, the dissolved oxygen is low and this indicates in greater pollution of the water sample.

Determination The BOD is based on the determination of dissolved oxygen over a period of 5 days. This is known as 5 day BOD test. A known volume of sample of sewage is diluted with a known volume of distilled water (water containing nutrients for bacterial growth). The dissolved oxygen is determined on the first day (D_1). This is kept for 5 days at 20°C in a stoppered bottle, away from light (incubation period). The dissolved oxygen is measured again after 5 days. The difference ($D_1 - D_2$) indicates the oxygen consumed in five days for oxidising the organic matter present in the water sample.

$$\text{BOD} = (D_1 - D_2) \times \text{dilution factor}$$

$$= (D_1 - D_2) \times \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

D_1 = Dissolved oxygen of diluted water sample immediately after preparation

D_2 = Dissolved oxygen of diluted water sample after incubation of 5 days at 20°C

Chemical Oxygen Demand (COD)

BOD is a measure of biodegradable organic impurities in water. It does not measure the non biodegradable matter. COD is a measure of both biodegradable and non biodegradable organic matter. Therefore, COD reveals the actual organic content present in water. *It is the amount of oxygen required by organic matter in a sample of water for its oxidation by a strong chemical oxidising agents such as $\text{K}_2\text{Cr}_2\text{O}_7$.*

Determination Organic matter is almost completely oxidised by a boiling mixture of chromic acid. A measured quantity (say 50 mL) of the sample is refluxed with a known excess of standard

potassium dichromate solution and dilute H_2SO_4 in the presence of $\text{Ag}_2\text{SO}_4 - \text{HgSO}_4$ as a catalyst. The amount of $\text{K}_2\text{Cr}_2\text{O}_7$ before the reaction and excess $\text{K}_2\text{Cr}_2\text{O}_7$ left after the reaction is determined by titrating against a standard ferrous ammonium sulphate solution (Mohr's salt) using ferroin as an indicator.

The difference between the $\text{K}_2\text{Cr}_2\text{O}_7$ originally present and that remaining unreacted gives the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ used for the oxidation of oxidisable impurities in water.

Volume of sample taken = 50 mL

Volume of 0.25 N FAS used in sample titration = V_1 mL

Volume of 0.25 N FAS used in blank titration = V_2 mL

Therefore volume of FAS equivalent to $\text{K}_2\text{Cr}_2\text{O}_7$ used for COD determination = $V_2 - V_1$ mL

Now,

$$\begin{array}{cc} N_1 V_1 & = & N_2 V_2 \\ \text{Sample} & \text{FAS} & \end{array}$$

$$N_1 \times 50 = 0.25 \times (V_2 - V_1)$$

$$N_1 = \frac{0.25(V_2 - V_1)}{50}$$

COD = Normality of water sample \times equivalent weight of oxygen

$$= \frac{0.25(V_2 - V_1)}{50} \times 8 \text{ g/L}$$

$$= \frac{0.25(V_2 - V_1)}{50} \times 8 \times 1000 \text{ mg/L}$$

$$= (V_2 - V_1) \times 40 \text{ ppm}$$

Solved Examples

1. 30 cm^3 of industrial effluent consumes 8 cm^3 of 0.05 N potassium dichromate solution. Calculate the COD of the effluent.

Solution

Volume of effluent = 30 cm^3

Volume of 0.05 N potassium dichromate consumed = 8 cm^3

COD = ?

Sample $\text{K}_2\text{Cr}_2\text{O}_7$

$$N_1 V_1 = N_2 V_2$$

$$N_1 = \frac{0.05 \times 8}{30}$$

COD = Normality of waste water sample \times equivalent weight of oxygen \times 1000

$$\text{COD} = \frac{0.05 \times 8}{30} \times 8 \times 1000 = 106.66 \text{ mg/L}$$

Ans COD of effluent sample = 106.66 mg/L

2. 50 cm^3 of acidified potassium dichromate was mixed with 50 cm^3 of a waste water sample and refluxed. 20.4 cm^3 of ferrous ammonium sulphate solution was required by unreacted acidified potassium dichromate solution. Blank titration was performed to estimate the amount of potassium dichromate at the beginning of the reaction. 50 cm^3 of acidified potassium dichromate requires 40.8 cm^3 of the same 0.2 N ferrous ammonium sulphate solution. Calculate the COD of waste water.

Solution

Volume of waste water = 50 cm^3

Volume of ferrous ammonium sulphate used for blank titration $V_1 = 40.8 \text{ cm}^3$

Volume of ferrous ammonium sulphate used for sample titration $V_2 = 20.4 \text{ cm}^3$

\therefore The volume of ferrous ammonium sulphate equivalent to $\text{K}_2\text{Cr}_2\text{O}_7$ used for oxidation of organic matter = $V_1 - V_2$

$$= 40.8 - 20.4 = 20.4 \text{ cm}^3$$

Normality of FAS = 0.2 N

Calculation of COD

$$N_1 V_1 = N_2 V_2$$

N_1 = Normality of O_2 in waste water; V_1 = volume of waste water

N_2 = Normality of FAS; V_2 = Volume of FAS used

$$N_1 \times 50 = 0.2 \times 20.4$$

$$N_1 = \frac{0.2 \times 20.4}{50}$$

$$\text{COD} = \frac{0.2 \times 20.4}{50} \times 8 \text{ g/L}$$

$$\text{COD} = \frac{0.2 \times 20.4}{50} \times 8 \times 1000 \text{ mg/L} = 652.8 \text{ mg/L}$$

Answer: COD = 652.8 mg/L

3. 30 cm³ of waste water is diluted to 600 cm³ and equal volumes are filled in two BOD bottles. A blank titration was performed using 100 cm³ of diluted waste water. It required 10 cm³ of 0.05 N sodium thiosulphate solution for neutralisation. 100 cm³ of the incubated sample was titrated again after 5 days. It required 5.0 cm³ of the same sodium thiosulphate solution. Calculate the BOD of waste water.

Solution

Initial volume of waste water = 30 cm³

Volume of diluted waste water = 600 cm³

Initially

Sample Na₂S₂O₃

$$N_1 V_1 = N_2 V_2$$

$$N_1 \times 100 = 0.05 \times 10$$

$$N_1 = \frac{0.05 \times 10}{100}$$

$$\text{Dissolved oxygen (D}_1\text{)} = \frac{0.05 \times 10}{100} \times \text{equivalent weight of O}_2 \times 1000$$

$$= \frac{0.05 \times 10}{100} \times 8 \times 1000 = 40 \text{ mg/L}$$

After 5 days

Sample Na₂S₂O₃

$$N_3 V_3 = N_4 V_4$$

$$N_3 \times 100 = 0.05 \times 5$$

$$N_3 = \frac{0.05 \times 5}{100}$$

$$\text{Dissolved oxygen after 5 days (D}_2\text{)} = \frac{0.05 \times 5}{100} \times \text{equivalent weight of O}_2 \times 1000$$

$$= \frac{0.05 \times 5}{100} \times 8 \times 1000 = 20 \text{ mg/L}$$

$$\text{BOD} = (D_1 - D_2) \times \frac{\text{Volume of sample after dilution}}{\text{Volume of sample before dilution}}$$

$$= (40 - 20) \times \frac{600}{30} = 400 \text{ mg/L}$$

Practice problems

- 20 cm³ of an industrial effluent consumed 4 cm³ of 0.5 N K₂Cr₂O₇ solution for oxidation. Calculate the COD of the effluent. [Ans 800 mg/L]
- 25 cm³ of sewage water for COD is reacted with 20 cm³ of potassium dichromate solution. The unreacted potassium dichromate requires 7.0 cm³ of 0.5 N ferrous ammonium sulphate solution under similar conditions. In blank titration, 12 cm³ of ferrous ammonium sulphate is used up. Calculate the COD of the sample. [Ans 800 mg/L]
- 25 cm³ of waste water sample is diluted to 500 cm³ and equal volumes are filled into two BOD bottles. In a blank titration 100 cm³ of waste water requires 8.8 cm³ of 0.02 N sodium thiosulphate solution. 100 cm³ of incubated sample after 5 days requires 4.2 cm³ of the same sodium thiosulphate solution. Calculate the BOD of the waste water. [Ans 147.2 mg/L]

Summary

- Water is the most important natural resource. It comprises of nearly 70% of the earth's surface. Out of this 70% water, 97% is in seas. Only 1% water is available as fresh water in lakes, rivers, streams etc
- Water is a very good solvent. It weathers rocks and minerals by dissolution, hydration, hydrolysis, carbonation and oxidation.
- Various organic, inorganic, gaseous and biological impurities are present in water.
- Hard water does not give lather with soap. Hardness is of two types
 - Temporary hardness – It can be removed by boiling and is due to the presence of bicarbonates of calcium and magnesium.
 - Permanent hardness – It is due to the presence of chlorides, sulphates and nitrates of calcium and magnesium. It cannot be removed by boiling.
- Degree of hardness is always expressed in terms of CaCO₃ as the molecular weight of CaCO₃ is 100 and it is highly insoluble.

$$\text{Degree of hardness} = \frac{\text{Weight of hardness producing substance} \times \text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of hardness producing substance}}$$

- Hardness can be expressed in various units like ppm, mg/L, degree Clarke and degree French.
 $1 \text{ ppm} = 1 \text{ mg/L} = 0.07^\circ \text{Cl} = 0.1^\circ \text{Fr}$
- Hard water generally causes four type of problems in boilers
 - (i) Scale and sludge formation
 - (ii) Boiler corrosion
 - (iii) Caustic embrittlement
 - (iv) Priming, foaming and carryover
- Scales and sludges are formed due to deposition of salts in boilers. Their formation can be prevented by various internal conditioning methods like carbonate conditioning, phosphate conditioning, aluminate conditioning and calgon conditioning or by physical methods like radioactive, electrical, colloidal conditioning.
- Hard water can be softened by lime soda process, zeolite process and ion exchange process.
- Water supplied for domestic use should be colorless, odorless, tasty, dissolved salt contents should be less, F^- , SO_4^{2-} , etc. should be as per prescribed limits
- The various steps of domestic (municipal) water supply include screening, sedimentation, filtration and disinfection of water.
- Sea water can be desalinated by various methods like reverse osmosis, electrodialysis, ultrafiltration and flash evaporation.
- Water can be defluorinated using the Nalgonda technique which involves addition of lime and alum followed by flocculation, sedimentation, filtration and disinfection.
- Waste water/sewage treatment includes collection, conveyance, treatment and disposal of treated water.
- After collection and conveyance of waste water it is treated in four steps:
 - Preliminary treatment or pretreatment: Its purpose is to remove the floating impurities from water and prevent further decay of sewage. Its steps are screening, presedimentation, microstraining, preaeration and prechlorination.
 - Primary treatment or physico-chemical treatment: It involves the removal of colloidal particles and other settleable impurities from sewage.
 - Secondary treatment or biological treatment: It is the removal of organic impurities in water with the help of bacterial mass. It is carried out either by trickling filter process or by activated sludge process.
 - Tertiary or advanced treatment: It is carried out for a very small fraction of water. It involves the removal of minerals like nitrogen and phosphorus and water is disinfected here.

- The various methods used for the determination of hardness are – O. Hehner's method, EDTA method and soap titration method.
- Parameters used to check the quality of water are dissolved oxygen, biological oxygen demand and chemical oxygen demand.

Review Questions

1. Define hardness of water. Differentiate between temporary and permanent hardness of water.
2. Explain the effect of water on rocks and minerals.
3. Define the various units of hardness. Write down the relationship between them.
4. What are scales and sludges, how are they formed in boilers? Also discuss the disadvantages of scales in boilers.
5. Write short notes on
 - (i) Boiler corrosion
 - (ii) Caustic embrittlement
 - (iii) Priming, foaming and carry over
 - (iv) Impurities in water
 - (v) Various conditioning methods for the prevention of scale in boilers.
6. Explain the lime soda process used for softening of hard water. Write down the chemical reactions involved in the process.
7. Explain the cold continuous and hot continuous lime soda process, which is better and why?
8. What is zeolite? How can it be used to soften water? What are the disadvantages of the zeolite process?
9. Explain the ion exchange process used to soften water. Why is it considered as the best method to soften the water?
10. What are the essential requirements of domestic water? Explain the various steps involved in the supply of water in a municipality or for domestic use.
11. Explain the term reverse osmosis. How can it be used to obtain fresh water from sea water?
12. Explain the following processes used to obtain soft water from sea water:
 - (i) Electrodialysis
 - (ii) Ultrafiltration
 - (iii) Flash evaporation
13. What is EDTA? Explain the determination of hardness using EDTA method.
14. How can you find out hardness of a given water sample using the soap titration method?

15. Explain the estimation of the following in water:
 - (i) Dissolved oxygen
 - (ii) Dissolved chlorides
 - (iii) Free chloride
16. What are BOD and COD? How can you estimate BOD and COD of a given water sample?
17. Explain the term reverse osmosis. How can it be used to obtain fresh water from sea water?
18. What are the effects of fluorine in water? Explain the Nalgonda technique for the defluoridation of water.
19. Write short notes on the following:
 - (i) Preliminary treatment or pretreatment of water
 - (ii) Primary treatment of water
 - (iii) Trickling filter process
 - (iv) Activated sludge process

Multiple Choice Questions

1. Amount of water available for human consumption is
 - (a) 1%
 - (b) 3%
 - (c) 97%
 - (d) 5%
2. Water causes weathering of rocks due to the following phenomenon
 - (a) Dissolution
 - (b) Hydration
 - (c) Hydrolysis
 - (d) All of the above
3. Hardness of water is due to
 - (a) K and Na salts
 - (b) Salts of iron
 - (c) Salts of Ca and Mg
 - (d) SiO_2
4. Permanent hardness is due to
 - (a) Carbonate of Ca
 - (b) Bicarbonate of Mg
 - (c) Chloride and sulphates of Ca and Mg
 - (d) None of the above
5. The most commonly used unit to express hardness is
 - (a) Degree French
 - (b) Degree Clarke
 - (c) ppm
 - (d) grains /gallon
6. Scale in boilers are formed due to
 - (a) Deposition of CaCO_3
 - (b) Deposition of CaSO_4
 - (c) Hydrolysis of magnesium salts
 - (d) All of the above
7. Excess nitrate in drinking water causes
 - (a) Anaemia
 - (b) Blue baby syndrome
 - (c) Irritation in skin
 - (d) Mouth blisters

8. The maximum permissible limit of fluoride in drinking water is
 - (a) 1.5 ppm
 - (b) 5 ppm
 - (c) 3 ppm
 - (d) 8 ppm
9. Lime soda process uses
 - (a) $\text{Ca}(\text{OH})_2$
 - (b) Na_2CO_3
 - (c) Both the above
 - (d) None of the above
10. Which process is not used for the desalination of water
 - (a) Reverse osmosis
 - (b) Lime soda process
 - (c) Electrodialysis
 - (d) Flash evaporation
11. Residual hardness in ion exchange process is
 - (a) 10-15 ppm
 - (b) 30-60 ppm
 - (c) 0-2 ppm
 - (d) 15-30 ppm
12. Alkalinity in water is due to
 - (a) OH^-
 - (b) CO_3^{2-}
 - (c) HCO_3^-
 - (d) All of the above
13. Which is not used for disinfection of water
 - (a) Chlorination
 - (b) Electrodialysis
 - (c) Ozonisation
 - (d) Addition of KMnO_4
14. Dissolved oxygen in water is determined by
 - (a) Mohr's method
 - (b) Gravimetric method
 - (c) Winklers method or iodometric titration
 - (d) EDTA method
15. Flash evaporation is a method of getting pure water from
 - (a) Sea water
 - (b) Industrial waste water
 - (c) Domestic sewage
 - (d) River water
16. Disinfection of water removes
 - (a) Salts from water
 - (b) Pathogenic bacteria from water
 - (c) Dissolved oxygen from water
 - (d) Hardness from water
17. Acceptable pH range for drinking water is
 - (a) 7 to 8.5
 - (b) 6 to 7
 - (c) 6.5 to 9.2
 - (d) 8 to 10
18. Which of the following is removed from water using Nalgonda technique
 - (a) Chlorine
 - (b) Fluorine
 - (c) Sulphates
 - (d) Hardness in water

19. The organic impurities from sewage are removed by

- | | |
|---------------------------|------------------------|
| (a) Preliminary treatment | (b) Primary treatment |
| (c) Secondary treatment | (d) Tertiary treatment |

Solution

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (a) | 2 (d) | 3 (c) | 4 (c) | 5 (c) | 6 (d) | 7 (b) | 8 (a) |
| 9 (c) | 10 (b) | 11 (c) | 12 (d) | 13 (b) | 14 (c) | 15 (a) | 16 (b) |
| 17 (a) | 18 (b) | 19 (c) | | | | | |

Chapter 3

CORROSION

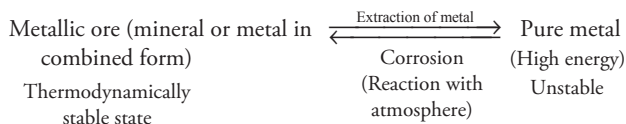
3.1 Introduction

We have all seen that when a piece of iron or an article made of iron is left in the open, it develops a reddish-brown coating. If this is left unattended for a long time, then the metal becomes weak and brittle and breaks off. A similar phenomenon is observed in copper that develops a greenish coating; similarly silver loses its luster and so on. Thus, metals degenerate in the presence of moisture and air. This is called corrosion, which may be defined as the process of spontaneous deterioration or disintegration of metals (except gold and platinum) caused by direct chemical or indirect electrochemical attack by reaction with the environment. Rusting of iron and formation of a green layer of basic carbonate on the surface of copper as discussed above are the common examples of corrosion. Note that the term rusting applies to the corrosion of iron and iron base alloys. Nonferrous alloys corrode but do not rust.

Why does corrosion occur?

Metals exist in nature in combined forms like oxides, sulphides, sulphates, carbonates, etc. These combined states (ores) are thermodynamically stable states of the metal. Energy is supplied to extract such metals from their ores. The extracted metal is at a higher energy level and hence it is in a thermodynamically unstable state. Metals try to get back to their stable states by combining with other elements, and in this process, corrosion occurs and oxides, sulphides, chlorides, sulphates, and so forth are formed.

Although corroded metals are thermodynamically more stable than pure metals, corrosion affects the useful properties of the metals like malleability, ductility and electrical conductivity.



3.2 Effects of Corrosion

The corrosion process, although slow, affects the metal drastically. The gravity of the problem can be realized by the fact that the approximate loss due to corrosion of metals is 2 to 2.5 billion dollars per annum all over the world. The common consequences of corrosion are as follows:

- (i) Corrosion causes severe economic losses and hampers the safety of equipment. It leads to direct economic losses that occur due to money being spent on maintenance and replacement of the corroded parts. Painting, maintaining cathodic protection devices, cost involved in protection techniques, such as galvanisation, modifying external environment by deaeration and dehumidification, all incur heavy financial losses.
- (ii) Metal loses its useful properties because of corrosion. It can become brittle, leading to the failure of machine parts.
- (iii) Frequent replacement and maintenance of the corroded parts leads to indirect financial losses, which include production loss during replacement and maintenance.
- (iv) Corroded pipes may lead to leakage of inflammable and toxic gases resulting in fire hazards; toxic gases lead to environmental pollution and affect the human and animal population adversely.
- (v) It causes contamination of the products. For examples traces of metals may alter the color of dyes. Food articles in corroded containers may get spoilt due to contamination.
- (vi) It has been estimated that nearly 25% of the annual production of iron is wasted because of corrosion.

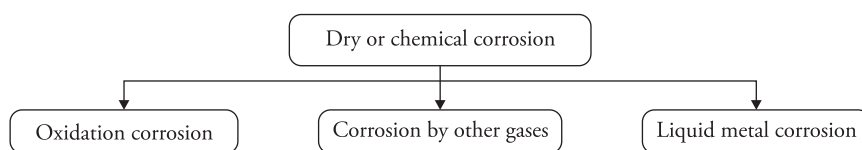
From the above discussion, it is clear that the study of corrosion and its prevention is essential for both engineers and metallurgists.

3.3 Theories/Mechanism of Corrosion

Several theories of corrosion have been proposed from time to time. The two basic theories of corrosion are

- Dry or chemical corrosion.
- Wet or electrochemical corrosion.

Dry or chemical corrosion Also called direct corrosion, it occurs because of direct chemical action of the environment on the metal surface in the absence of moisture or a liquid electrolyte. It generally occurs at a temperature higher than 100 °C when it is not possible to develop a surface water layer. It is generally of three types:

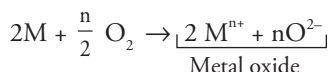


- (a) **Oxidation corrosion** It is brought about by the direct action of oxygen on the metal surface at high or low temperature. At low temperature, alkali and alkaline earth metals are oxidized and at high temperatures except Ag, Au and Pt, all other metals are oxidized. It generally takes place in the absence of moisture. For example, copper oxidizes in air at a low temperature of about 260 °C forming a film of Cu_2O . At temperatures between 260 °C and 1025 °C the

Cu_2O layer is overlaid by a layer of CuO film. Similarly, iron oxidizes at a low temperature of approximately 250°C , forming an oxide consisting mainly of Fe_3O_4 .

Mechanism The metal surface reacts directly with oxygen forming an oxide layer. This oxide layer acts as a barrier and prevents further oxidation of the metal. For further oxidation to take place, either the metal must diffuse outward through the oxide layer or oxygen must diffuse inward. Both the transfers occur, but the outward diffusion of the metal ion is faster as the size of the metal ion is smaller than that of the oxygen atom or the O^{2-} ion.

Chemical reactions involved



For corrosion to continue further, the nature of the oxide film is very important. They are of four types

- (i) **Stable** It is fine grained, tightly sticking and impervious, for example, Al, Sn, Pb and Cu. It acts as a protective layer and prevents further corrosion.

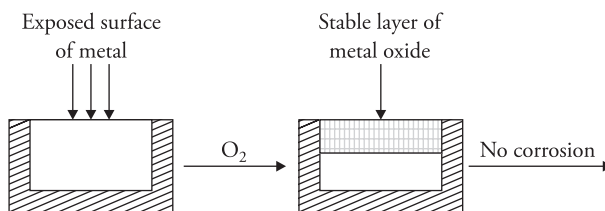


Figure 3.1 Stable oxide layer

- (ii) **Unstable** The oxide formed decomposes back into metal and oxygen, for example, Ag, Pt and Au. As a result, there is no corrosion.

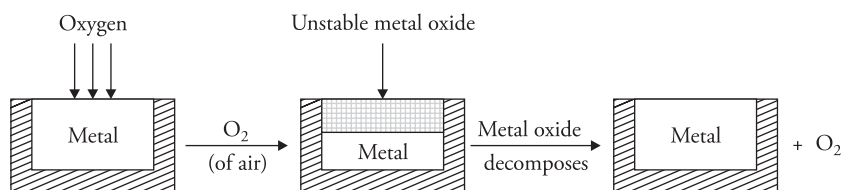
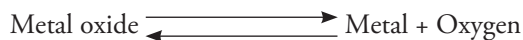


Figure 3.2 Unstable oxide layer

- (iii) **Volatile** The oxide layer formed volatilizes as soon as it is formed. Fresh metal surface is exposed for further attack. This causes rapid and continuous corrosion, for example, molybdenum.

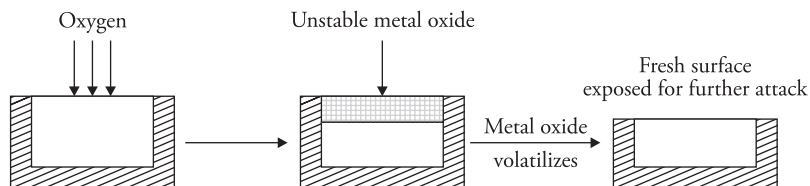
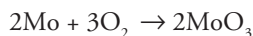


Figure 3.3 Volatile oxide layer

- (iv) **Porous** The oxide film is porous, that is, having pores or cracks. Here the O_2 penetrates inside and attacks the underlying metal and hence continuous corrosion occurs, for example, iron and steel.

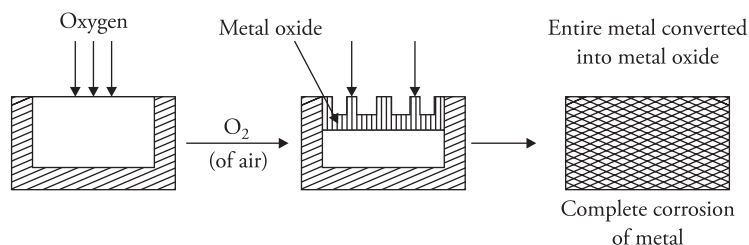


Figure 3.4 Porous oxide layer

The extent of protection given by the oxide film or the corrosion product to the underlying metal is governed by the *Pilling–Bedworth Rule*. In fact it is the parameter that helps to predict the extent of corrosion of a metal.

Definition If the volume of the oxide film is *less* than the volume of metal laying underneath then the oxide layer is porous, contains cracks and hence is nonprotective, and if the volume is *equal to or greater than* the volume of the underlying metal, the oxide film is continuous, nonporous and protective, that is, further corrosion does not take place.

For example, Case I Li, Na, K, Mg, Ca, Sr, etc.

Case II Al, Cu, etc.

The ratio of the volume of metal oxide to the volume of the underlying metal is called the Pilling–Bedworth ratio or the specific volume ratio. This ratio helps to predict the extent of corrosion of a metal. Greater the value of Pilling–Bedworth ratio, lesser is the extent of corrosion. Table 3.1 gives the Pilling–Bedworth ratio for a few metal oxides. The table shows that the Pilling–Bedworth ratio for oxides of calcium and magnesium are 0.6 and 0.8, and hence they are nonprotective, whereas

aluminium with a Pilling–Bedworth ratio of 1.3 forms a protective oxide film. Similarly the Pilling–Bedworth ratios for W, Cr and Ni are 3.6, 2.0 and 1.7, respectively, and hence corrosion will be least in tungsten as its Pilling–Bedworth ratio is the highest.

Table 3.1 Metal oxide Pilling –Bedworth ratio

Metal	Metal oxide	Pilling –Bedworth ratio
Tungsten	WO ₃	3.6
Chromium	Cr ₂ O ₃	2.0
Cobalt	CoO	1.9
Titanium	TiO ₂	1.8
Iron	FeO	1.7
Copper	CuO	1.7
Nickel	NiO	1.7
Aluminium	Al ₂ O ₃	1.3
Magnesium	MgO	0.8
Calcium	CaO	0.6
Lithium	Li ₂ O	0.6

- (b) **Corrosion by other gases** In this, dry gases like H₂, Cl₂, F₂, SO₂ and CO₂ directly attack the metal surface. Rate of corrosion depends upon the chemical affinity between the metal and gas and also on the nature of the film formed.

For example,



The AgCl film is nonporous and protective (volume of the film > volume of the metal) and thus it protects the metal from further attack.



SnCl₄ being volatile, Sn undergoes excessive corrosion. The rest of the mechanism is the same as that of oxidation corrosion.

(iii) H₂S attacks steel forming FeS layer, which is porous in nature.

- (c) **Liquid metal corrosion** It occurs when an anhydrous liquid attacks the metal surface. When a liquid metal flows over a solid metal at high temperature it weakens the solid metal because of

- Its dissolution in liquid metal.
- Penetration of liquid metal into solid metal. For example, sodium metal (coolant) leads to the corrosion of cadmium in a nuclear reactor.

Wet or electrochemical corrosion

This type of corrosion occurs under wet or moist conditions, and is more common than dry corrosion. It occurs when

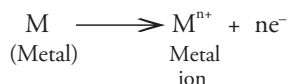
- (i) A metal is in contact with a conducting liquid or
- (ii) When metals of different reactivities are in contact with a solution.

Rusting of iron is the most common example of electrochemical corrosion. The following conditions must be fulfilled for the formation of electrochemical cell.

- (i) There must be separate anodic and cathodic areas.
- (ii) There must be electrode potential between the anode and cathode.
- (iii) There must be a metal path connecting the anode and cathode.
- (iv) Conducting liquid should be present between the two electrodes.

Once the above conditions are fulfilled a “corrosion cell” is formed and corrosion takes place as discussed below. The reactions taking place at the anode and cathode are as follows.

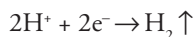
- (a) **Anodic reactions** Oxidation occurs at the anode; the metal loses electrons and passes them into the solution. Thus, the metal at anode is destroyed by dissolving or by changing into metal ions. *Hence, corrosion always occurs at the anodic areas.*



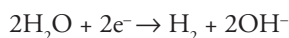
- (b) **Cathodic reactions** The electrons released at the anodic areas are consumed in the reactions at the cathode. Depending on the nature of the environment, the cathodic reactions are of two types

- (i) *Evolution of hydrogen* This mechanism usually occurs when
 - anodic areas are large and cathodic areas are small and
 - oxygen is absent.

When the environment is acidic, H^+ ions of the acid take up electrons and hydrogen gas is evolved.



In neutral and alkaline medium, the reaction will be

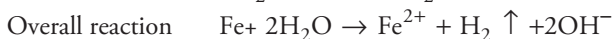
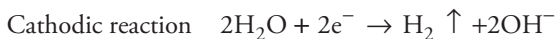


For example, rusting of iron takes place in acidic medium in the absence of oxygen as follows



The Fe^{2+} ions react with the anion of the acid to form the corrosion product.

In neutral or alkaline medium, the following reactions occur



The Fe^{2+} formed at the anode and OH^- formed at the cathode diffuse towards each other and meet to form $\text{Fe}(\text{OH})_2$

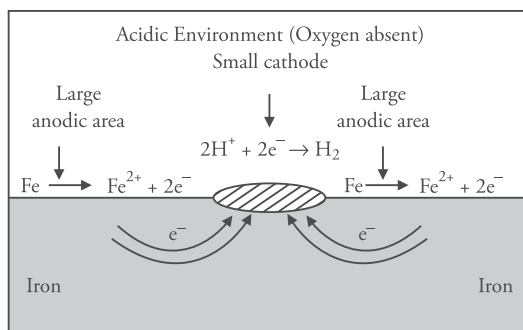


Figure 3.5 (a) *Electrochemical/wet corrosion by hydrogen evolution (in acidic environment)*

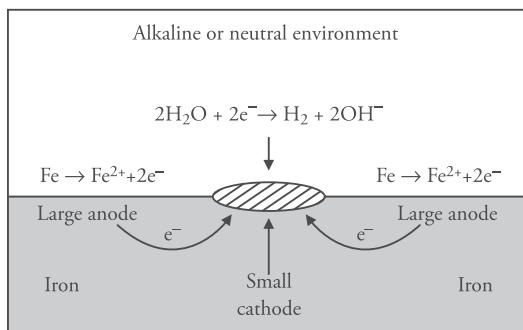
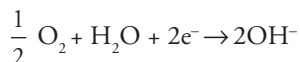


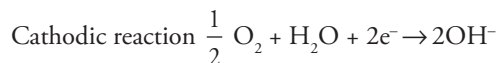
Figure 3.5 (b) *Electrochemical/wet corrosion by hydrogen evolution (in neutral or alkaline environment)*

Absorption of oxygen This mechanism occurs when

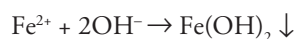
- Anodic areas are small and cathodic areas are large.
- Oxygen is present and the environment is neutral or alkaline.



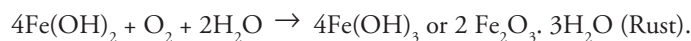
Example The above mechanism occurs in neutral aqueous solution in the presence of atmospheric oxygen. The surface of iron is always coated with a thin layer of iron oxide. When the film cracks, small anodic areas are formed, while the metal coated with the oxide layer acts as the cathode. The following reactions occur:



The Fe^{2+} ions (at anode) and OH^{-} ions (at cathode) diffuse, and when they meet, ferrous hydroxide is precipitated.



$\text{Fe}(\text{OH})_2$ is not stable, and in the presence of oxygen and moisture, it oxidizes as follows:



$\text{Fe}(\text{OH})_3$ corresponds to rust, which is hydrated iron(III) oxide of variable composition $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. The degree of hydration of iron (III) oxide affects the color of rust that may vary from black (Fe_3O_4) anhydrous magnetite to yellow reddish brown ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

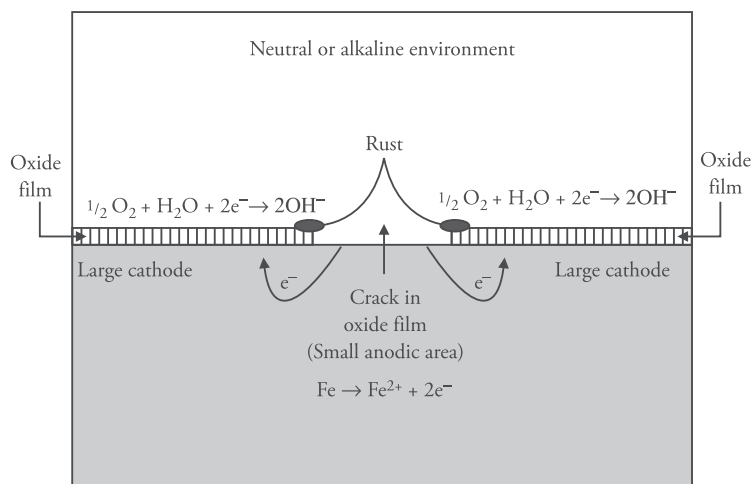


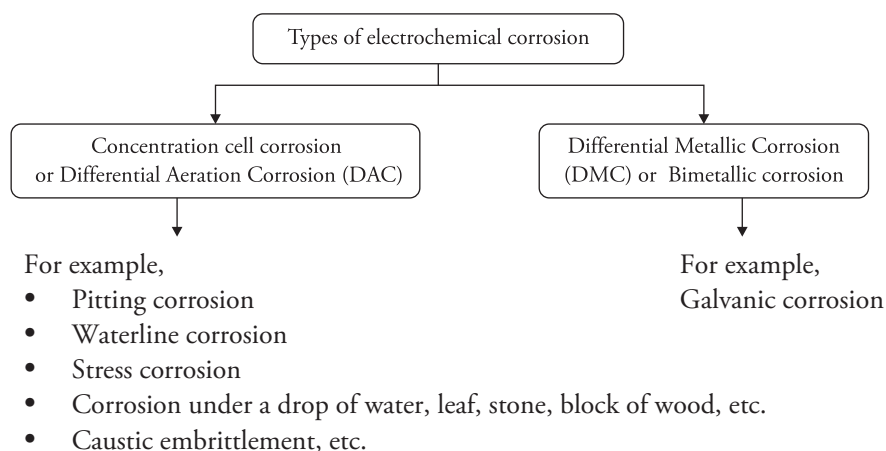
Figure 3.6 *Electrochemical corrosion by oxygen evolution process (in neutral or alkaline environment)*

It is important to note that, although corrosion occurs at anode, the corrosion product is formed closer to the cathode. This is because the smaller Fe^{2+} ions produced at anode diffuse rapidly toward cathode as compared with the diffusion of larger OH^{-} ions toward the anode.

Table 3.2 Difference between chemical corrosion and electrochemical corrosion

S.No	Chemical corrosion	Electrochemical corrosion
1	It takes place in dry conditions	Presence of aqueous solution or electrolyte is a must
2	It takes place by direct chemical attack of the environment on the metal	It takes place indirectly by the formation of electrochemical cells
3	It can take place on a homogenous and heterogeneous surface	It takes place on heterogeneous metal surfaces only
4	Corrosion product deposits at the same spot where corrosion has occurred	Corrosion occurs at the anode but the corrosion product deposits near the cathode
5	Corrosion occurs uniformly	Nonuniform corrosion takes place

3.4 Types of Corrosion



*Corrosion also occurs by the formation of differential temperature cells. In these cells the electrodes are made of the same metal each of which is at different temperature immersed in a common electrolyte. Such cells are generally formed inside heat exchangers, boilers, immersion heaters, etc although the working of these cells is not clearly understood.

1. **Galvanic corrosion** It is also called bimetallic corrosion or differential metallic corrosion. It occurs when two dissimilar metals (for example, Zn and Cu) are electrically connected and exposed to an electrolyte and then the metal higher in the electrochemical series undergoes corrosion.

For example, if Zn and Cu are connected, Zn acts as anode and undergoes corrosion, whereas Cu acts as cathode (Fig. 3.7).

Mechanism: In a Zn – Cu couple

(At anode) $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

The reaction at the cathode depends upon the environment.

Acidic environment $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$ (evolution of hydrogen)

Alkaline or neutral environment $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (absorption of oxygen)

Zn^{2+} and 2OH^- ions interact to form $\text{Zn}(\text{OH})_2$. Hence, Zn dissolves and Cu is protected.

The common examples of galvanic corrosion are as follows

- Use of Cu pipes in conjunction with iron pipes in water distribution system.
- A steel propeller shaft in a bronze bearing.
- Steel screw in brass marine hardware.
- Lead–antimony solder around Cu wire.

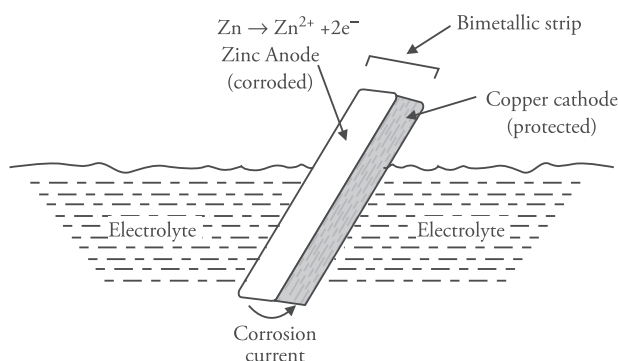


Figure 3.7 Galvanic corrosion

2. **Concentration cell corrosion** Concentration cell corrosion takes place when different areas of a metal surface are in contact with an electrolyte of different concentration (caustic embrittlement) or varying aeration (pitting corrosion, waterline corrosion, corrosion under a block of wood or a drop of water, etc). The difference in electrolyte/air concentration may be because of local temperature differences or inadequate stirring or slow diffusion of metal ions.

Differential aeration corrosion (DAC) This is the most common type of concentration cell corrosion. It occurs when one part of the metal is exposed to a different air concentration than the other. There will be a difference of potential between differently aerated areas. Experimental observations have shown that

- Poorly oxygenated areas become anodic and
- Highly oxygenated areas become cathodic.

Corrosion occurs at the anode. Some common examples of differential aeration corrosion are cited below

- (a) **Waterline corrosion** If a Zn metal is partially immersed in a neutral solution (say NaCl) and the solution is not stirred, the parts above and close to the waterline are well aerated and act as cathode. Areas deep inside the solution are anodic, as the concentration of oxygen is less. Thus, a potential develops that causes a flow of current between two areas of the same metal. Zn dissolves at the anodic area (Fig. 3.8 a).

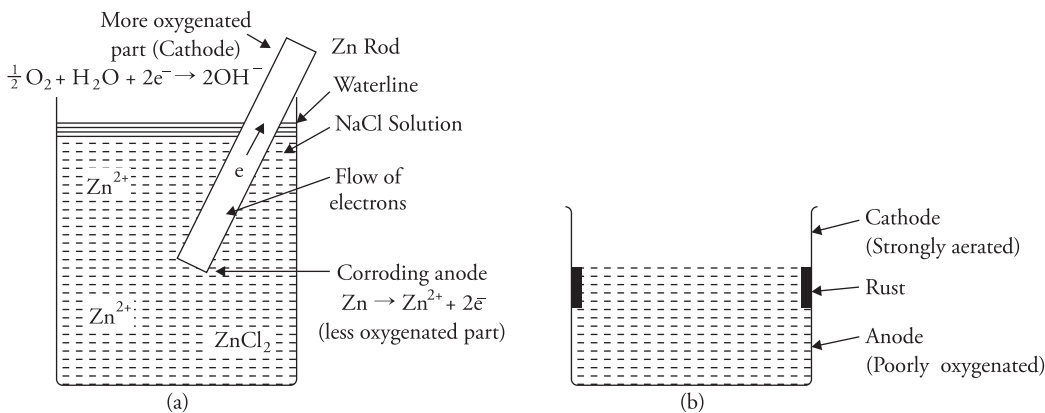
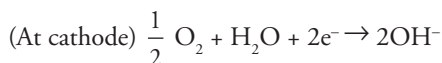
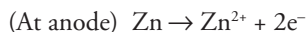
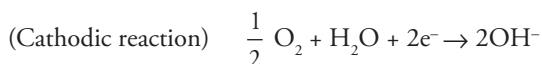
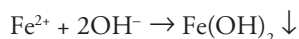


Figure 3.8 Waterline corrosion

Similarly, you must have observed rusting along a line just beneath the level of water stored in an iron tank. This is also waterline corrosion and is because of differential aeration. The area just above the waterline is well aerated and acts as cathode, whereas the areas below the waterline are poorly aerated/oxygenated and hence become anodic and get corroded. The reactions at anodic and cathodic areas are



The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and when they meet ferrous hydroxide is precipitated (Fig. 3.8 b).



- (b) **Pitting corrosion** It is also an example of differential aeration corrosion. It is a localised type of corrosion and occurs in areas of pits, cavities and pinholes that penetrate deeply within the metals (Fig. 3.9). The pit is oxygen deficient and acts as anode, whereas the plane surface is oxygen-rich and acts as cathode. As the area of anode is small the rate of corrosion will be high. Anodic metal dissolves and the pit gradually deepens resulting in the weakening of the metal in these areas. If the pits are small they may be covered by corrosion products. Therefore, it is difficult to detect pitting corrosion till sudden failure of the metal occurs.

Pitting of metal generally occurs because of breakdown or cracking in the protective film on the metal surface at specific points. It may be due to scratches, surface roughness, chemical attack, stresses and strains, etc.

Pitting is common in aluminium alloys, copper alloys, stainless steels and some nickel alloys. Pits are initiated by activating ions like chloride ions. Pits may be shallow or deep. Iron buried in soil generally corrodes by the formation of shallow pits whereas stainless steel immersed in sea water corrodes with the formation of deep pits.

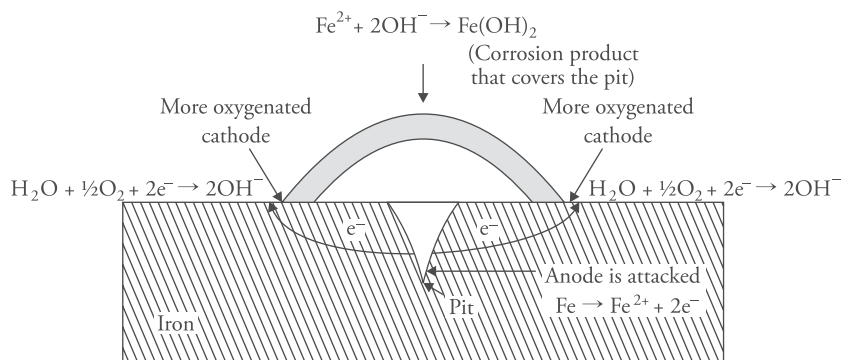


Figure 3.9 Pitting corrosion

- (c) **Drop Corrosion or Corrosion under a block of wood, leaf, metal, stone, etc** If a drop of electrolyte solution, block of wood, leaf, metal or stone is in contact with a metal surface, rusting occurs in the central region beneath the drop, block of wood, leaf, metal or stone. The area around these objects is oxygen-rich and hence becomes cathodic, whereas the central region beneath these objects is poorly oxygenated/aerated and hence becomes anodic (Fig. 3.10). At this region, Fe^{2+} is oxidized to Fe^{3+} and gets corroded. (For equations refer waterline corrosion).

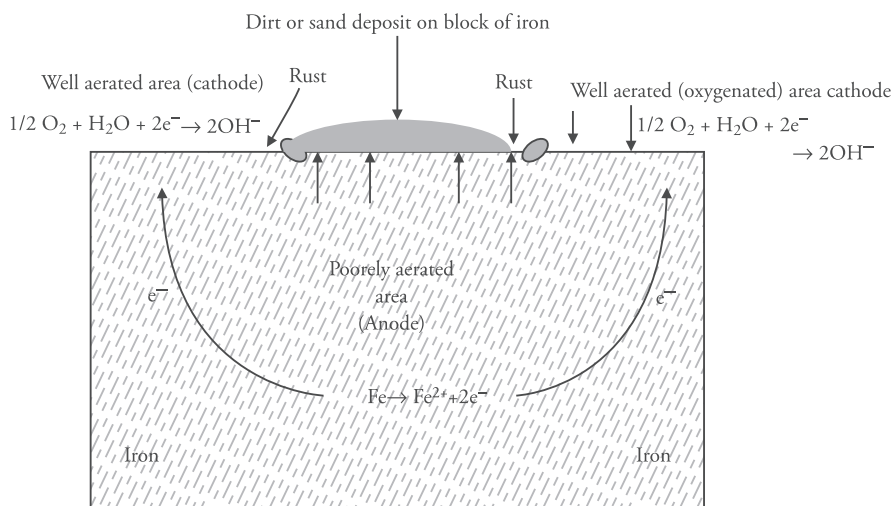


Figure 3.10 Mechanism of differential aeration corrosion

(d) **Stress corrosion (season cracking)** It occurs because of the combined effect of

- Static tensile stress and
- Corrosive environment near the metal.

The metals develop internal stress during manufacture process like fabrication, heat treatment, rolling, insufficient annealing, etc. Thermodynamically, areas under stress are at higher energy level. Therefore, they have high electrode potential and act as anode. The stress-free areas are at lower electrode potential and act as cathode (Fig. 3.11). The difference in potential of these two is quite low and corrosion is concentrated in small path that is anodic. The anodic area becomes highly reactive and is attacked even by a mild corrosive environment, resulting in the formation of a crack. Examples of stress corrosion are

- Caustic alkalis and strong nitrate solution for mild steel. When mild steel under stress is exposed to hot concentrated alkaline or hot concentrated nitrate solutions (like boiling 60% $\text{Cr}(\text{NO}_3)_2 + 3\% \text{NH}_4\text{NO}_3$) it cracks along the intergranular path by stress corrosion cracking.
- Underground steel pipelines used for transmitting oil and gas are under high internal pressure and hence fail by stress corrosion cracking. Intergranular cracking of stressed steel also occurs when steel is in contact with $\text{SbCl}_2 + \text{HCl} + \text{AlCl}_3$ in a hydrocarbon solvent.

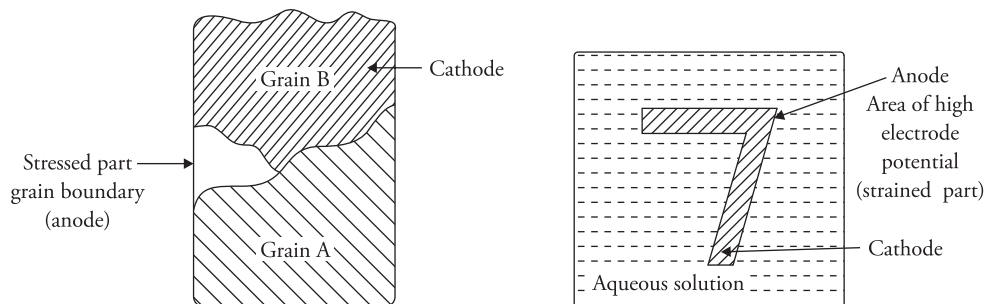


Figure 3.11 Stress corrosion

Examples of stress corrosion are as follows

- Season cracking in brass** It is a term that applies specifically to stress corrosion in brass (copper alloy). Pure copper is immune to stress corrosion but the presence of alloying agents like Zn, Al, P and Sb makes it prone to stress corrosion. Brass undergoes intergranular cracking in an atmosphere having traces of NH_3 . The orientation of atoms in adjacent grains of brass is different and hence it becomes highly reactive. They react with NH_3 forming $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$, respectively. Brass dissolves, initiating a fissure that later forms a crack in the presence of high tensile stress. This can be avoided by avoiding contamination of air with NH_3 .
- Caustic embrittlement** It is corrosion in boilers due to excess NaOH . Inside the boiler the riveted areas, and areas of bends and joints are under great stress and hence undergo corrosion. The mechanism has already been discussed in detail in the chapter on water (Chapter 2) under the section boiler troubles with hard water.

Stress corrosion can be prevented by severe cold working, heat treatment (annealing and quenching), use of special alloys (steel containing small amount of aluminium, titanium or niobium plus tantalum show resistance to stress corrosion).

- (e) **Crevice corrosion** It is produced at gaps in the region of contact between metals with metals or nonmetals. The gaps are very narrow so that the liquid penetrates in them and stagnates. It occurs at crevice between different metallic objects such as bolts, rivets, washers, nuts, etc. Supply of oxygen is restricted in the areas of the crevices; hence, differential aeration corrosion takes place. The areas of the crevice become anodic and undergo corrosion (Fig. 3.12). Corrosion is further accelerated by the deposition of dirt, scales, debris, etc. Crevice corrosion is affected by several metallurgical, physical and environmental factors, the most important being the crevice gap.

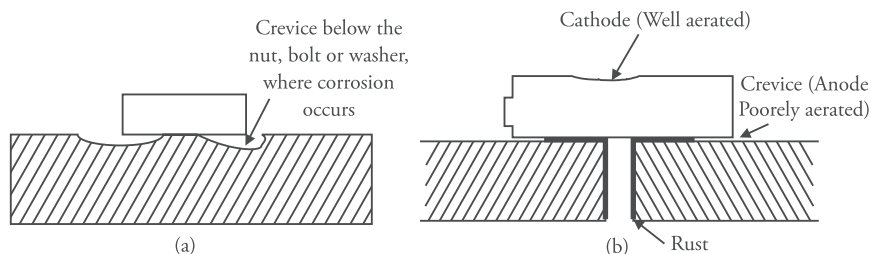


Figure 3.12 Crevice corrosion

In case aluminium component (nut, bolt) and steel parts are coupled together in, say, sea water, then both galvanic and crevice corrosion will occur and then it can be termed as *galvanic crevice corrosion*. The rate of such corrosion will be very high. Use of butt welds instead of overlap joints help to prevent crevice corrosion. In case overlap joints cannot be avoided then they should be sealed by continuous welds.

- (f) **Intergranular corrosion** This type of corrosion occurs along the grain boundaries. When a metal is solidified, the solidification starts at a number of randomly distributed nuclei within the molten mass. Each of them grows in a regular pattern or atomic array to form grains. Because of random distributions of the nuclei, the planes of atoms in adjacent grains do not match and these mismatched areas between adjacent grains are known as grain boundaries.

Certain compounds precipitate along the grain boundaries. The precipitated compounds as well as the grain centers behave as cathode, whereas the grain boundaries behave as anode (Fig. 3.13). Owing to the precipitation of certain compounds at the grain boundaries the solid metal solution adjacent to the boundary becomes depleted in those constituents. Thus, a potential difference is created leading to the corrosion at the anodic grain boundaries.

Alloys are generally more susceptible to intergranular corrosion. Stainless steel is an alloy of iron, carbon and chromium. During its welding, chromium carbide gets precipitated at the grain boundaries like stainless steel and those based on nickel, aluminium, magnesium, copper and zinc. Thus, the chromium composition is less in the grain center and the region at the grain boundaries adjacent to the precipitate. The chromium-depleted region becomes more anodic with respect to the solid solution in the grain, which is rich in chromium. The corrosion proceeds along the grain boundary and continues until the affected grain is completely dislodged. This type of corrosion causes sudden failure of the material (without any warning) due to loss of cohesion between the grains. Aluminium copper alloys are also attacked by this type of corrosion. Intergranular corrosion can be prevented by proper heat treatment followed by rapid quenching to avoid the heterogeneous precipitation that usually takes place due to slow cooling.

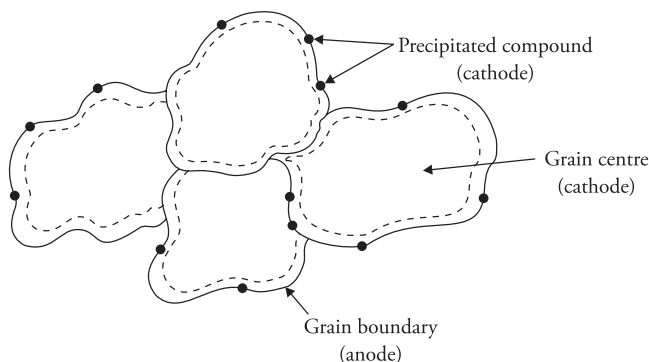


Figure 3.13 Intergranular corrosion

(g) **Soil corrosion** It is also called underground corrosion. There are various factors responsible for the corrosiveness of the soil. Some of them are

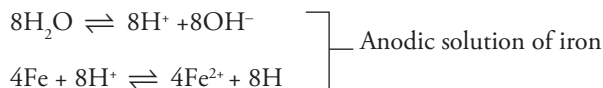
- Acidity of soil (soils containing organic acids derived from humus are quite corrosive to steel, zinc, lead and copper).
- Moisture of the soil
- Electrical conductivity
- Electrolytes (dissolved salts)
- Degree of aeration (porosity)
- Presence of bacteria and microorganisms.

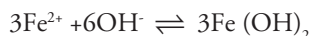
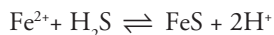
Underground structures like water mains, cables, etc. passing from one soil to the other suffer from corrosion because of differential aeration in different parts of the soil. The presence of electrolytes enhances the rate of corrosion. Certain types of bacteria that oxidize organic matter and produce gases also cause soil corrosion. Soil corrosion is purely electrochemical in nature. If the soil is acidic the mechanism of corrosion is similar to the hydrogen evolution process.

Soil corrosion can be prevented by organic and inorganic coatings, metallic coatings, soil alteration by surrounding the metal structure by limestone chips and by the use of various cathodic protection methods.

(h) **Microbiological corrosion** This type of corrosion causes deterioration of metal directly or indirectly by microbes such as bacteria, algae, moulds or fungi. Depending upon whether the microorganisms thrive in the presence or absence of air they can be aerobic and anaerobic microorganisms.

Anaerobic conditions Corrosion of iron and steel is caused by sulphate-reducing microorganisms (*Desulfovibrio desulphuricans*), which grow in anaerobic conditions. These microorganisms grow in the pH range 5–9 with temperatures between 20 °C and 30 °C and require sulphates for their nourishment. The microbiological corrosion of iron takes place as follows





The corrosion products are ferrous hydroxide $\text{Fe}(\text{OH})_2$ and black iron sulphide.

Aerobic conditions

Aerobic bacteria such as sulphur microorganisms like bacteria of the group *Thiobacillus* oxidize the sulphur present in their cells to sulphuric acid, which is responsible for corrosion and attack on iron. Moreover, these aerobic bacteria consume oxygen, thereby decreasing the oxygen content on the medium in contact with the metal structure. This causes differential aeration corrosion at the metal surface. Similarly, aerobic bacteria like *Ferrobacillus ferrooxidans* directly oxidize iron into iron oxide or hydroxide and cause the formation of precipitates of ferric hydroxides.

3.5 Passivity

It is defined as the phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series. In an electrochemical series, the metals are arranged from top to bottom in the order of their increasing reduction potentials (or decreasing reactivities). The metal placed higher in the series is more reactive than the one placed below it. Hence, the metal that is placed higher in the electrochemical series behaves as an anode and undergoes corrosion. For example, Zn corrodes faster than Fe, which in turn corrodes faster than Sn. This is because Zn is placed above Fe, which in turn is placed above Sn in electrochemical series.

However, there are some exceptions. Ti, which is above Ag in the electrochemical series, is less reactive than Ag. Similarly, in a Zn–Al couple, Zn which is below Al in the electrochemical series, is corroded. These observations are opposite to those predicted by the electrochemical series. This is because Ti and Al develop strongly adhering oxide layers on their surface, thereby making their effective electrode potential more positive (or less negative). These metals are said to be rendered passive.

Passivity is because of the development of a highly protective, very thin (0.004-mm-thick) invisible oxide film on the surface of the metal. The film so formed makes the metal behave as a noble metal. The presence of ample excess oxygen on the metal surface favours passivation. Common examples of passivation are

- Metals like Cr, Al, Ni, Ti and a wide variety of stainless steel alloys containing Cr show outstanding corrosion resistance in oxidizing environment. These metals and alloys form insoluble oxide films on their surface in the presence of oxygen and are rendered passive. On changing the environment, i.e., in reducing environment these metals become chemically active and undergo rapid corrosion.
- Iron is readily attacked by dilute HNO_3 but in concentrated acid it forms a very thin protective film and becomes passive or inactive.
- Al becomes passive in concentrated HNO_3 due to the formation of thin protective oxide film.

Table 3.4 Electrochemical series versus galvanic series

S.No	Electrochemical series	Galvanic series
1	Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration, without any oxide film on them	This series was developed by studying the corrosion rates of metals and alloys in different environments like sea water without removing their oxide films if any
2	The position of metal is fixed in the electrochemical series	The position of metal may shift in the galvanic series depending on the environment
3	It gives no information regarding the position of alloys	Alloys have also been included and hence their corrosion rates can be studied from this series
4	This series comprises metals and nonmetals	This series comprises metals and alloys
5	It predicts the relative displacement tendencies	It predicts the relative corrosion tendencies

3.7 Factors Influencing Corrosion

The rate and extent of corrosion depend on the following

- Nature of the metal
- Nature of the corroding environment.

Nature of the metal

Corrosion rate depends on the properties of the metal

- Position in the galvanic series** When two metals or alloys are in contact in the presence of an electrolyte, the metal that is higher in the galvanic series undergoes corrosion. The rate and severity of corrosion depends on the difference in their position. Greater the difference in the position of the two metals greater is the corrosion of the anodic metal.
- Purity of the metal** Pure metals are less prone to corrosion. Impurities in a metal cause 'heterogeneity' and forms minute/tiny electrochemical cells, where the anodic part gets corroded. For example, very pure and smooth zinc metal will not corrode in very pure hydrochloric acid. However, zinc metal containing impurities of Fe and Pb corrodes rapidly. The figures below show the effect of impurities on corrosion of aluminium by hydrochloric acid.

% Aluminium	99.998	99.97	99.2
Relative corrosion rate	1	1000	30,000

However it is incorrect to assume that pure metals do not corrode at all . For example in water saturated with air high purity iron corrodes at almost the same rate as impure commercial iron . This is because corrosion depends on several other factors like variation in temperature, availability of oxygen to different parts of the metal which leads to the setting up of local action cells.

- (iii) **Physical state of the metal** Rate of corrosion is greatly influenced by the physical state of the metal like particle size, orientation of grains, localised stresses, smooth or rough surface, etc. Smaller the grain size greater will be the corrosion; similarly, areas under stress, even in a pure metal, are likely to be anodic and corrosion takes place at these areas.
- (iv) **Nature of surface film** In the presence of air, all metals are covered with a thin film of metal oxide. The ratio of the volume of metal oxide to that of the metal is called “*specific volume ratio*.” If the specific volume ratio of the metal is greater than one the metal will be protected from corrosion, and if the specific volume ratio is less than unity the film will be unstable and the underlying metal will be corroded (Pilling–Bedworth rule). The specific volume ratios of Ni, Cr and W are 1.7, 2.0 and 3.6, respectively. Consequently, the rate of corrosion of W is the least even at high temperatures.
- (v) **Relative areas of anodic and cathodic parts** Rate of corrosion is high if anodic areas are small and cathodic areas are large. This is because the current density at smaller anodic areas is much greater. Moreover, if the cathodic areas are large, then it will demand more electrons, which will be met by the brisk and rapid corrosion of the anodic area. For example, in copper plates (cathode) with steel (anode) rivets, the steel rivets are almost completely corroded because the smaller steel rivets are coupled to larger copper cathodic area.
- (vi) **Solubility of corrosion products** Corrosion is faster if the corrosion product is soluble in the corroding medium. If the corrosion product is insoluble in the corroding medium, or it reacts with the corroding medium to form insoluble product; the product acts as a physical barrier and suppresses further corrosion. For example, the corrosion of Pb in H_2SO_4 proceeds at a much slower rate due to the formation of insoluble PbSO_4 .
- (vii) **Volatility of the corrosion product** If the corrosion product is volatile, it leaves the surface as soon as it is formed, leaving the underlying metal surface exposed for further attack. This causes rapid, continuous and excessive corrosion. MoO_3 is the volatile corrosion product formed on the oxidation of Mo. It volatilizes, causing extensive corrosion of the underlying metal.

Nature of the corroding environment

Environmental factors have a vital role in deciding the rate of corrosion. The major environmental factors that affect corrosion are as follows

- (i) **Temperature** As the rate of all chemical reactions increases with the rise in temperature, rate of corrosion also increases as temperature rises. At higher temperatures, even the passive metal can become active and get corroded. However, differential aeration corrosion slows down at higher temperatures. This is because of the faster diffusion of O_2 into pits and crevices. Moreover, corrosion also occurs due to the formation of differential temperature cells.
- (ii) **Humidity** Corrosion increases with the increase in humidity of the atmosphere. The effect of humidity on corrosion of enameled steel is given in the table below.

Relative humidity	0–65	65–80	80–90	100
Corrosion (appearance)	No corrosion	Thin corrosion filaments	Wide corrosion filaments	Blisters due to corrosion

This is due to the fact that moisture acts as a solvent for O_2 , H_2S , SO_2 , NaCl , and so on to furnish the electrolyte for setting up a corrosion cell.

Common examples,

- Atmospheric corrosion of Fe is slow in dry air compared with moist air. Steel parts left in desert areas remain bright and tarnish free for very long periods of time.
 - Gases like H_2S and SO_2 dissolve in water and increase the acidity of medium and hence increase the corrosion rate.
 - Solids like NaCl dissolve in water to increase its conductivity and hence increase the rate of corrosion.
- (iii) **Presence of impurities in atmosphere** Gases like H_2S , SO_2 and CO_2 increase acidity of the liquid closer to the metal surface and hence increases the rate of corrosion. Salts like NaCl present in marine environment increase the conductivity of the electrolyte, thus speeding up the corrosion process. Presence of even trace amount of H_2S in atmosphere tarnishes silver (due to formation of Ag_2S) and copper (due to formation of a mixture of $\text{Cu}_2\text{S} + \text{CuS} + \text{Cu}_2\text{O}$)
- (iv) **Effect of pH** Generally, acidic media ($\text{pH} < 7$) are more corrosive than alkaline or neutral media. However, amphoteric metals like Al, Zn, Pb form complexes in alkaline medium.
- (v) **Nature of ions present**
- Presence of ions like silicate ions in the medium leads to the formation of insoluble products (like silica gel), which inhibit further corrosion.
 - Chloride ions present in the medium destroy the protective and passive film, thereby exposing the fresh metal surface for further corrosion.
 - Iron undergoes rapid corrosion in an environment containing ammonium salts.
 - Presence of traces of copper or any other noble metal in mine waters accelerates the corrosion of iron pipes used for carrying these waters.
- (vi) **Conductance of the corroding medium** Conductance of the corroding medium has a vital role in corrosion. Dry sandy soils have lower conductance compared with clay or mineralized soils. Hence, metallic structures buried under clay or mineralized soils undergo corrosion faster than under dry sandy soils.
- (vii) **Formation of oxygen concentration cell** Owing to differential aeration “oxygen concentration cell” is set up and the anodic parts having less oxygen concentration suffers corrosion. The corrosion by differential aeration has already been discussed in detail.

3.8 Protection against Corrosion (Corrosion Control)

The various methods by which corrosion can be controlled and prevented are as follows

1. Protection by proper designing
2. Material selection
3. Modifying the environment
4. Modification of properties of the metal
5. Use of inhibitors
6. Cathodic protection or electrochemical protection
7. Use of protective coating.

A. **Protection by proper designing** Corrosion can be prevented by using proper design. Important design principles are as follows

- (i) Avoid direct contact of two dissimilar metals in a corroding medium. If it cannot be avoided then use an insulating fitting between them to avoid direct metal–metal electrical contact. For example, metal washers should be covered with plastic washers to avoid direct contact between the two metals.
- (ii) When two dissimilar metals in direct contact are to be used then
 - They should be as close as possible in the galvanic series.
 - The anodic material should have a large area and the area of cathodic material should be as small as possible.
 - The screws, bolts, nuts and welds should be of less reactive metals so that they can act as cathode with small area.

For example, copper rivets are used to fasten steel sheets and not vice versa because copper is nobler than steel and hence acts as a cathode. Owing to the small area of the cathode, the cathodic reaction is limited and corrosion of anodic steel proceeds slowly.

- (iii) Joints should be welded with same metal/alloy (Fig. 3.14a). Riveting or bolting with other metal results in crevice corrosion.

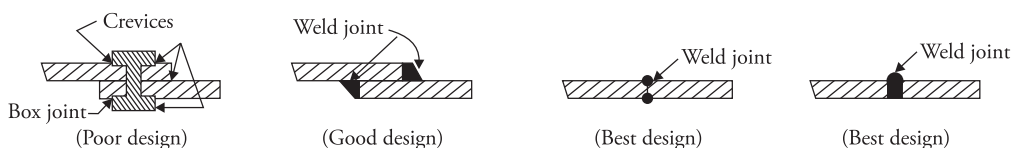


Figure 3.14 (a) Prevention of corrosion by use of proper joints

- (iv) As moisture has an important role in corrosion, the design should be such that moisture retention is as low as possible. Sharp corners should be avoided and storage containers should be designed in such a way that they can be completely drained and cleaned (Fig. 3.14 b).

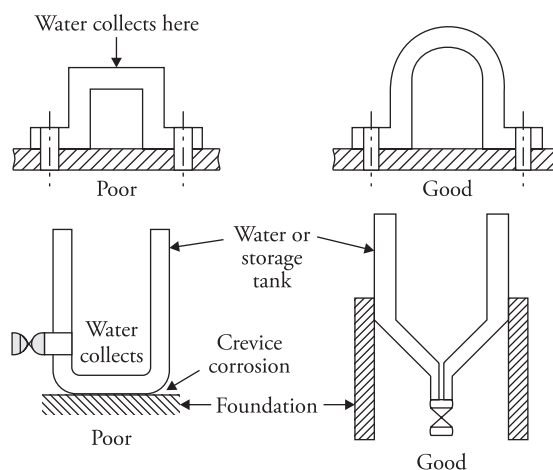


Figure 3.14 (b) Corrosion control by design modification

Sharp corners should be avoided because dust and solid particles accumulate leading to differential aeration corrosion (Fig. 3.14 c).

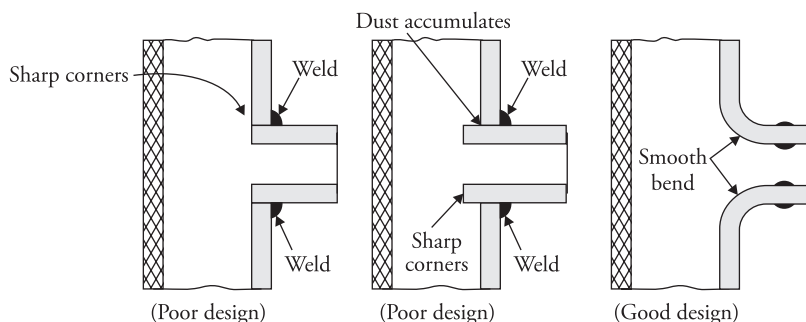


Figure 3.14(c) *Prevention of corrosion by elimination of sharp corners and stresses*

- (v) Wherever possible, equipment should be supported on legs to allow free circulation of air otherwise corrosion will occur due to differential aeration (Fig. 3.15).

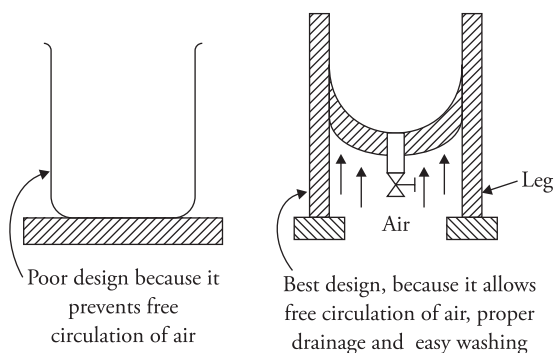


Figure 3.15 *Prevention of corrosion by use of proper design*

- (vi) The anodic metal should not be painted or coated. Any scratches in coating may cause rapid localised corrosion.

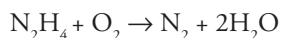
B. Material selection

- (i) **Using pure metals** Impurities in metals cause heterogeneity that leads to corrosion. Pure metal is less prone to corrosion. However, pure metals are expensive and are usually weak and do not possess the required strength.
- (ii) **Using metal alloys** The metals can be made corrosion-resistant by alloying them with suitable alloying elements. For example, chromium is used as alloying metal for iron and steel as it produces an exceptionally coherent oxide film, which protects the steel from further corrosion.

C. Modifying the environment

The corrosive nature of the environment can be reduced by

- (i) *De-aeration* Removal of gases like oxygen and carbon dioxide from the environment reduces corrosion.
- (ii) *Deactivation* It involves addition of chemicals that remove oxygen. For example, addition of Na_2S , Na_2SO_3 or hydrazine removes O_2 .



- (iii) *Dehumidification* Alumina or silica gel may be added to remove moisture from the environment.
- (iv) *Alkaline neutralisation* The acidic substances in the environment (like H_2S , CO_2 , SO_2 , etc) can be neutralised by adding bases like NH_3 , NaOH , lime, etc.

D. Modification of the properties of the metal

The properties of the metals can be modified to decrease the effects of corrosion. The properties can be modified by

- (i) *Alloying* Alloys are more resistant to corrosion than pure metals.
- (ii) *Refining* As pure metals are more corrosion-resistant, refining can increase the corrosion resistance of the metal. The amount of S and P in steels and C in stainless steels is reduced by refining.
- (iii) *Annealing* It is a heat treatment given to the metals to reduce residual stress.

- E. **Use of Inhibitors** A substance that when added to the corrosive medium effectively decreases the corrosion of the metal is known as a corrosion inhibitor.

Inhibitors are of two types

- (i) *Anodic inhibitors* They get adsorbed on the anodic surface forming a passive film on it (example chromates, phosphates, tungstates, etc.), thereby decreasing the corrosion rate.
- (ii) *Cathodic inhibitors* They slow down the reactions taking place at the cathode (i.e., H_2 evolution in acidic medium). For example, organic inhibitors like amines, mercaptans, substituted ureas and thioureas, heavy metal soaps, etc, decrease the H_2 evolution process by decreasing the diffusion of H^+ ions considerably.

Inhibitors like Mg, Zn or Ni salts react with the hydroxyl ions at the cathode forming corresponding hydroxides that deposit at the cathode and decrease the O_2 absorption process.

F. Cathodic Protection or Electrochemical Protection

The principle involved is that the metal to be protected is made to behave like a cathode. Alloys/metals like steel, brass, copper and lead can be protected in all types of soils and almost all sorts of aqueous media by cathodic protection method. This technique is also employed to prevent pitting corrosion in stainless steel or aluminium and can also be used to prevent stress corrosion cracking in brass, mild steel, stainless steel, magnesium and aluminium. This can be done in two ways

- (i) **Sacrificial Anode Cathodic Protection Method (SACP)** In this method, the metal structure to be protected is connected to a more reactive metal. For example, if an iron structure is to be protected it is connected to a more reactive metal like Zn or Mg. The more reactive metal behaves as an anode and the iron structure becomes cathodic (Fig. 3.16). Thus, the iron structure is protected and the anode undergoes corrosion. After sometime, the anode is corroded completely and is replaced with a fresh anode. This anode (Zn or Mg), which is sacrificed to protect the base metal is called the *sacrificial anode* and the method is called *sacrificial anode cathodic protection method*. This type of protection method is used in industry to protect buried pipelines, underground cables, ship hulls and even in railway tracks.

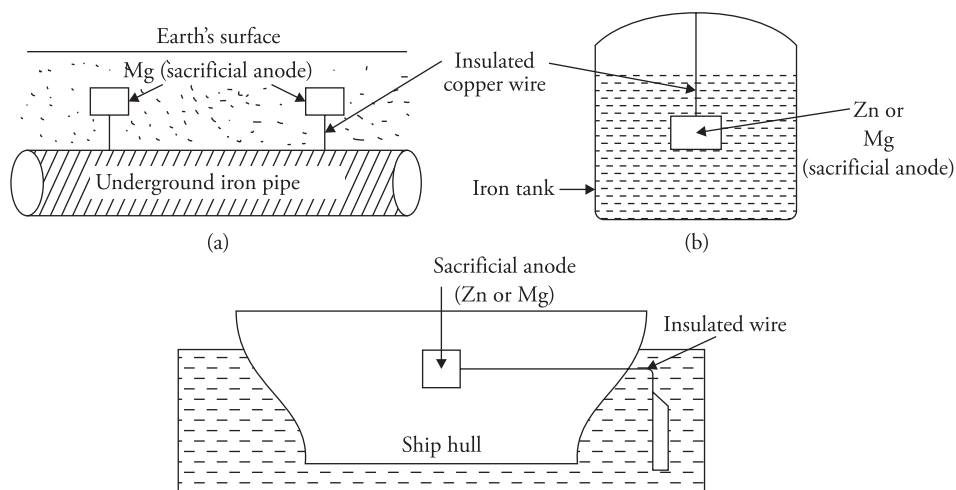


Figure 3.16 Sacrificial anodic protection

- (ii) **Impressed current cathodic protection (ICCP):** In this method direct current from an external source is impressed (applied in opposite direction) to nullify the corrosion current and convert the corroding metal from anode to cathode. The positive terminal of the direct current source is connected to the anode and the negative terminal to the structure to be protected. Anode is made of inert material like graphite, carbon, stainless steel and is buried in a backfill like gypsum to increase electrical contact between itself and the surrounding soil (Fig. 3.17).

Applications

- Ships and submarines are protected against corrosion by connecting the surface to negative terminal of DC generator.
- Water tanks, buried oil or water pipelines, transmission line towers are protected by this method.
- Canal gates, off shore oil drilling structures, bridge decks, parking garages are also protected by this method.

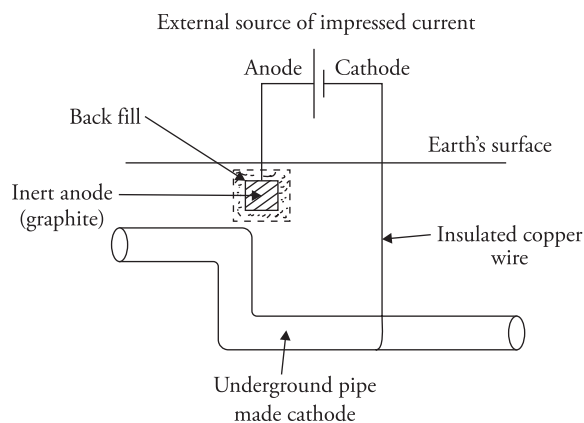


Figure 3.17 *Impressed current cathodic protection*

- G. **Anodic protection** Anodic protection is applicable to the metals like aluminium which become passive by the deposition of oxide films. Similarly titanium which becomes passive in the presence of chloride ions can be protected by anodic protection method even in a solution of HCl. By an externally impressed anodic current, a protective passive film is deposited on the metal surface. Metals like Fe, Cr, Ti and their alloys can be made passive by the application of controlled anodic currents and the corrosion rate can be decreased. Anodic protection method is not applicable to metals like zinc, magnesium, cadmium, silver, copper or copper based alloys.
- H. **Use of protective coatings** The metal structure to be protected is covered with metallic or nonmetallic coatings. The metallic coatings often used are zinc, tin, nickel, chromium, aluminium, copper, etc. These coatings separate the base metal from the corrosive environment and protect the base metal from corrosion.

Metallic coatings

- (i) **Anodic coatings** These coatings are sacrificial coatings in which the base metal (metal to be protected) is coated with a more reactive metal so that the coating metal behaves as an anode and undergoes corrosion in preference to the base metal. For example, coating of Zn on Fe (galvanisation) (Fig. 3.18). The advantage of anodic coating is that if a scratch or pore appears on the coating metal then a galvanic cell is formed between the coating metal and the base metal, and the coating metal is corroded and the base metal is protected. The rate of corrosion is lower comparatively because the area of anode is much larger as compared with the area of the cathode.

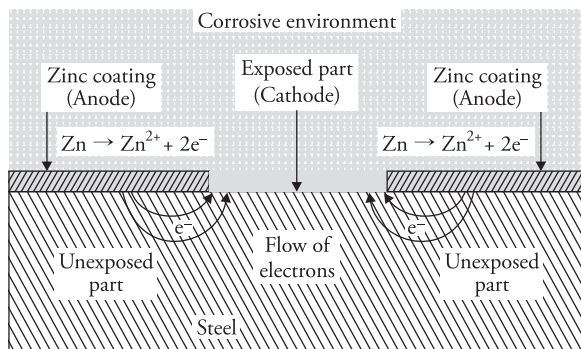


Figure 3.18 Functioning of anodic coating (galvanisation)

- (ii) **Cathodic coatings** It is coating of a noble or less reactive metal on the base metal. The coating metal is corrosion-resistant and hence provides only barrier protection to the base metal. What is important to note is that if the coating metal develops a crack or develops pores then the base metal being more reactive will undergo corrosion. For example, coating of Sn on iron (tinning) (Fig. 3.19). The rate of corrosion here is high because the anodic area is small and the cathodic area is large. Therefore, such coatings are effective only when the coating is continuous and free from pits and cracks.

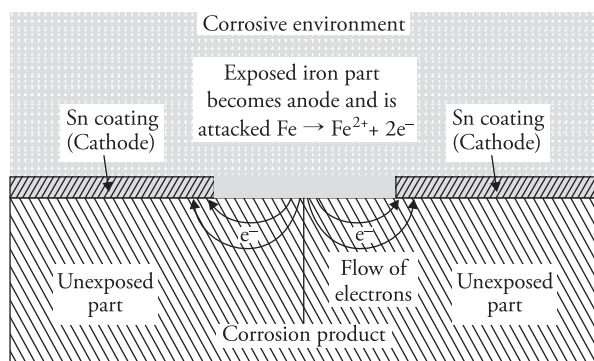


Figure 3.19 Functioning of cathodic coating (tinning)

Table 3.5 Comparison between anodic coating and cathodic coating

S.No	Anodic coating	Cathodic coating
1	It protects the base metal 'sacrificially'	It protects the base metal due to its greater corrosion resistance or a noble character
2	Electrode potential of the coating metal is lower than that of the base metal	Electrode potential of the coating metal is higher than that of the base metal
3	If pores, cracks or discontinuities develop on the base metal, even then the base metal is not corroded till the entire coating metal is consumed	If pores, cracks or discontinuities develop on the base metal, the base metal is corroded rapidly
4	Example coating of Zn on iron (galvanisation)	Example coating of Sn on iron (tinning)

3.9 Methods of Application of Metal Coatings

A. **Hot dipping** In this method, the base metal is immersed in a bath of molten metal, covered by a molten flux layer (usually zinc chloride). The flux cleans the base metal and prevents oxidation of the molten coating metal. Galvanisation and tinning are the most common examples using hot dipping method.

- (i) **Galvanising** The process of coating iron and steel articles with a thin coat of zinc to prevent them from rusting is called galvanisation. For this, the article to be coated is first cleaned with dilute H_2SO_4 solution (7–8%) for about 15–20 minutes at 60–90 °C. This process is called *pickling*. Pickling removes dust, rust, scale, oxide layer and other impurities. It is then followed by preliminary treatment in which the article is treated with 5% HF to dissolve sand particles on the surface of the article. Any other superficial oxide if present is cleaned by passing the article through a 5–20% solution of zinc ammonium chloride. The article is then washed, dried and dipped in a bath of molten zinc, maintained at 425–430 °C. The surface of the bath is covered with a flux of ammonium chloride to prevent the formation of oxide. The article coated with zinc layer is then taken out and passed through rollers to remove excess zinc and produce thin film of uniform thickness. It is then annealed at a temperature of 650 °C and then cooled slowly (Fig. 3.20).

Uses For coating iron sheets, wires, pipes, bolts, screws, buckets, etc, it may be noted here that zinc gets dissolved in dilute acids to form toxic compounds. Hence, galvanised utensils cannot be used for storing food articles.

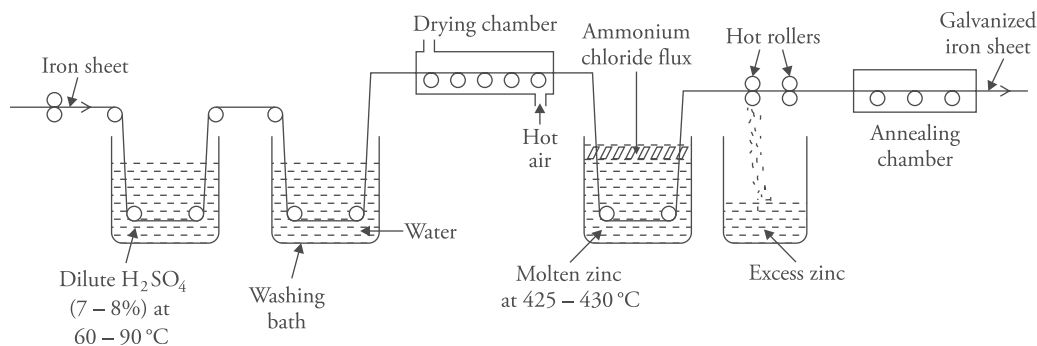


Figure 3.20 Process of galvanising

- (ii) **Tinning** It is the process of coating iron or steel articles with tin. As done above, the iron or steel article is cleaned by pickling with dilute H_2SO_4 solution (5–8%) to remove impurities like dust, rust, scale or any oxide film. It is then passed into a zinc chloride flux that helps the molten metal to stick to the metal sheet. The sheet passes through a tank containing molten tin and finally through a series of rollers immersed in baths containing palm oil. The palm oil protects the tin-coated surface against oxidation.

Rollers help to remove excess tin and produce a thin film of uniform thickness. Palm oil is removed from the surface by absorption in bran or saw dust and then these are brushed off and the sheets are polished with dry flannel rollers (Fig. 3.21).

Uses Because of the nontoxic nature of tin, tinning is widely used for coating steel, copper and brass sheets used for manufacturing containers for storing food articles. Tinned copper sheets are used for making utensils.

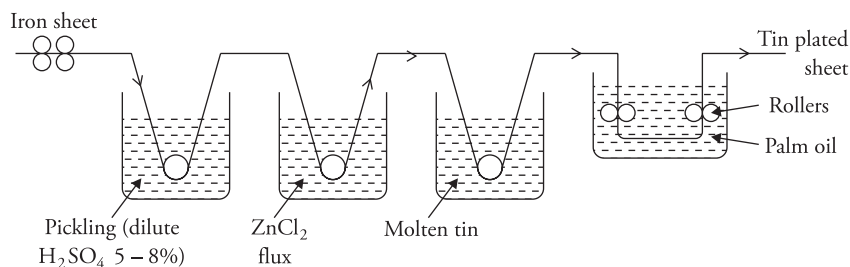


Figure 3.21 Tinning

- B. **Electroplating** In this method, the metal to be plated is made cathode and placed in a bath containing the ions of the metal to be deposited. The anode is either inert or made of the coating metal. When current is passed, the coating metal ions migrate and get deposited in the form of a thin layer. For example, plating of silver on a spoon (details refer sec 3.10).
- C. **Metal cladding** In this method, the base metal is sandwiched between two layers of the protecting metal. It is then passed through rollers under the action of heat and pressure so that these layers adhere to the base metal. The cladding materials used are corrosion-resistant like nickel, copper, silver, lead, platinum, etc. Cladding material should be anodic to the base metal. Cladding is used for protecting aluminium alloys and for combining the strength of steel wire with copper having high electrical conductivity. Alclad sheeting is prepared by sandwiching a plate of duralumin between two layers of 99.5% pure aluminium and it is widely used in aircraft industry.
- D. **Spraying** This type of coating is applied to finished structures and is accomplished by spraying a stream of 'atomized' droplets of molten metal onto the roughened surface of the metal to be protected, with the help of a spraying gun.

Before spraying, the surface is prepared with sharp sand blast. The molten metal is then sprayed. The sprayed coatings are continuous with very little pores and a sealer or paint is applied on such a coating to provide a smooth surface finish.

The advantages of metal spraying are

- It increases the speed of working.
- It can be easily applied to large irregular surface and on nonmetallic surfaces like glass, wood, plastic, etc.

However, it is important to note that the adhesion strength of the coating obtained by metal spraying is less than that obtained by hot dipping or electroplating. For better results, the surface must be properly cleaned and roughened. Sprayed coating are applied by two techniques

- *Wire gun technique* In this method, the coating metal is melted by an oxy-acetylene flame and then sprayed by a blast of compressed air.
- *Powder metal technique* In this technique, an aspirator sucks the powdered metal in the powder chamber and it is then heated as it passes through the flame of the blow pipe. The metal disintegrates forming a cloud of molten globules or flakes that are adsorbed on the surface of the base metal. Metals with low melting point like lead, zinc, tin and aluminium can be easily coated by this technique.

Nonmetallic coatings

Nonmetallic coatings may be organic or inorganic.

1. **Organic coatings** They are inert organic barriers that provide corrosion resistance as well as embellish it. Organic coatings include paints, varnishes, enamels and lacquers, etc.

(a) Paints

They are most commonly used for the prevention of corrosion. A paint consists of the following

- (i) *Pigment* It is the solid substance that is the essential constituent of the paint. The pigment imparts color to the paint, improves the permeability of the paint to moisture, increases its weather resistance and provides strength to the paint.
 - (ii) *Binder* It is the film forming component of the paint and is commonly called the vehicle. The common binders are natural and synthetic resins like acrylics, polyurethanes, polyesters, epoxy resins or oils. They provide adhesion and affect properties like durability and glossiness. The paints also contain oil that evaporates from the surface after the application of the paint.
 - (iii) *Thinners* Thinners help in adjusting the viscosity of the paint. Commonly used thinners are turpentine oil, mineral spirits, benzene, naphtha, xylol, kerosene and ketones like acetone.
 - (iv) *Fillers* They impart toughness to the paint and increase its durability. Commonly used fillers are barytes (BaSO_4), talc, asbestos, dolomite clay, calcium sulphate, etc.
 - (v) *Plasticizers* They provide plasticity to the paint and minimize cracking. Common plasticizers are tricresyl phosphate, triphenyl phosphate, tributyl phthalate, etc.
- (b) **Varnishes** They can be considered as paints without pigment. They contain a resin and dry to form a hard transparent film. The other constituents of varnish are drying oil, drier and a volatile solvent.

The resins in varnishes are natural resins like shellac, kauri, etc, and synthetic resins like polyurethane, urea formaldehyde, alkyds and epoxy resins. Linseed oil, castor oil and

soyabean oil are used as the drying oils. Driers like linoleates, naphthenates, resinates of Pb, Co and Mn enhance the drying rate of the oil constituents. Turpentine oil and petroleum spirit are used as thinners.

Applications

They are used for protection against corrosion. Varnish is generally applied over the paint to improve the appearance and give a glossy finish.

- (c) **Enamels** Enamel paints are paints that dry to give a hard glossy finish. They are generally used for outdoor coatings that are exposed to sunlight and subjected to changes in temperature. They contain resins like alkyd resin, pigments like titanium dioxide and calcium sulphate mixtures. They are oil-based but these days water-based enamels are also used. Enamels are also prepared by adding varnish to oil-based paints.
- (d) **Lacquers** A lacquer consists of a colloidal dispersion of cellulose derivatives like cellulose nitrate, cellulose acetate, resin like alkyd, phenol-aldehyde and a plasticizer in solvents and diluents.

Lacquers are used for interior decoration; due to their resistance to abrasion and cracking they are used on automobile bodies.

2. **Inorganic coatings** Inorganic coatings form chemical bonds with the base metal and provide protection against oxidation at high temperature, weathering and corrosion. The commonly used inorganic coatings are phosphate coatings and chromate coatings.

- (i) **Phosphate coating** It is a coating of metal phosphate like manganese phosphate, iron phosphate and zinc phosphate on steel parts and ferrous metals to improve their corrosion resistance and is also applied as foundation coating and serves to prepare the surface before applying paints. These coatings can also be applied on aluminium, zinc, cadmium, silver and tin surfaces.

For the application of phosphate coatings, iron, zinc and manganese phosphate salts are dissolved in a solution of phosphoric acid. The metal to be coated (steel or iron) is placed in this solution and the pH of the solution is raised. As the phosphate salts are less soluble at high pH, increasing the pH reduces their solubility and they deposit on the metal surface.

- (ii) **Chromate coating** Like phosphate coating, these coatings also provide the base for paints. These coatings are formed by the reaction between the base metal with sodium dichromate and dilute sulphuric acid. At a particular pH, basic chromium chromate ($\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) gets precipitated on the metal surface. The primary function of chromate coating is to render the base metal passive, thereby acting as a corrosion inhibitor. They are applied on aluminium, zinc, cadmium, copper, silver, manganese and tin metal substrates.

Inorganic coatings can also be glass linings, vitreous enamels and porcelain enamels fused on the metals. Iron and steel water pipes are protected by Portland cement coatings on them. Interior of oil tanks and chemical storage tanks are also lined with Portland cement coatings. These coatings offer good corrosion resistance but they cannot withstand thermal and mechanical shocks.

3.10 Electroplating

Electroplating is the process of deposition of a metal on a metal, nonmetal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.

In this method, the base metal to be coated or electroplated is made the cathode and the coating metal is made the anode. The process of electroplating consists of two steps.

- (i) **Surface preparation** In this step, the surface of the metal to be electroplated is cleaned by several chemical and mechanical methods.
- (ii) **Electrodeposition** In this step, the coating metal is electroplated over the base metal.

1. Surface cleaning

Before electrodeposition on the base metal, its surface has to be cleaned to remove any scale, dirt, rust, oxides, etc. The various methods employed for cleaning the metal surface are as follows

- (i) *Mechanical cleaning* In this method the metal surface is cleaned mechanically with hand. The loosely bound impurities like rust and dust particles are removed with the help of an abrasive such as sand and detergent along with brush scrapper, etc. The hard and adherent impurities are removed by using knife scrappers, grinding wheel, cutters, dull chisels, etc. After removing the impurities, the metal surface is washed with hot water and the surface is polished and buffed to remove surface defects like scratches.
- (ii) *Solvent cleaning* In this method, oils, fatty substances and greases are removed from the metal surface by using solvents like tetrachloroethylene, perchloroethylene, carbon tetrachloride, naphtha, acetone, xylene, etc. The metal surface is further cleaned with hot water or steam containing wetting agents and alkalies. This treatment provides a metal surface readily wetted by aqueous solution and ready for electroplating.
- (iii) *Alkali cleaning* It is used for removing greases, oil and water-soluble impurities. In this method, the metal surface is cleaned with the help of alkaline solution of sodium carbonate, sodium hydroxide, sodium silicate or trisodium phosphate containing soaps and wetting agents. After alkali treatment, the surface is washed thoroughly with water and then treated with 1% chromic acid solution to neutralise the last traces of alkali. Alkali solutions are more effective at elevated temperature of 60–90 °C. Effectiveness can further be increased by passing electric current and making the metal cathodic in alkaline solution. This method is particularly useful for removing coating of paint from the metal surface.
- (iv) *Pickling and etching* Pickling is used to remove oxides and scales from the metal surface by immersing the object in a bath containing a suitable solvent. Etching uses a strong acid or mordant to clean the metal surface. Pickling is carried out either in an acidic or in an alkaline bath. HCl or H₂SO₄ (10%–30% by volume) is employed for acidic pickling and 50%–80% NaOH is used for alkaline pickling. After pickling the surface should be neutralised and dried immediately. Inhibitors are added to the pickling bath to protect the metal. Aluminium is pickled in alkaline solution. Pickling agents for some common metal surfaces are as follows

Table 3.6 Pickling agents for some common metal surfaces

Metal	Pickling agent
Chromium plating	H_2SO_4
Copper, brass, nickel	Dilute HNO_3 or mixture of dilute HNO_3 and dilute H_2SO_4
Steel	Warm dilute H_2SO_4 or cold HCl
Aluminium	Alkaline solution (50%–80% NaOH)

- (v) **Sand blasting** In this method, sand is introduced into the air stream under a pressure of 25–100 atmospheres and the blast is influenced on the surface to be cleaned. As a result of the sand-blast impact, any scale present on the surface of the metal is removed. Sand blasting is generally employed to remove oxide scales; however, acid pickling and etching give better results. The greatest disadvantage of this method is that it is injurious to health and leads to silicosis in the workers; moreover, the process requires expensive equipments.

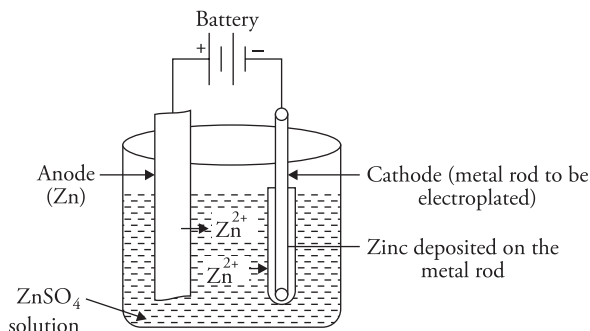
Surface preparation is a very important step before electroplating because efficient cleaning provides a smooth surface for electrodeposition and the deposit obtained is tough, adherent, smooth and bright in appearance.

2. **Electrodeposition** It is the process of depositing the desired metal on the surface of the other metal. It is done after proper cleaning of the metal surface to remove oils, grease and other impurities.

Process of electroplating

After surface preparation, the cleaned article is made cathode of the electrolytic cell and is hung on racks placed on the cathode bar. The anode consists of either

- The metal to be deposited and then immersed in the electrolyte containing the ions of the anode material say if zinc is to be coated then the electrolyte must contain zinc ions (like solution of ZnSO_4) (Fig 3.22).

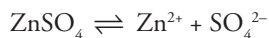
**Figure 3.22** Electroplating of zinc over metal rod

- An inert material like graphite or lead–antimony alloy and immersed in the electroplating bath containing solution with ions of metal to be electroplated.

The anode and cathode are dipped in suitable electrolytic solution and direct current is passed. If needed, the electroplating bath can be heated either by passing steam or with the help of immersion electric heaters. Similarly, cooling is done with water in pipes or coils placed inside the bath or tank outside it. Under the influence of electric current, the metal ions migrate to the cathode and get deposited on it. The cathode is moved gradually or rotated slowly to ensure uniform deposition of the metal on the cathode.

Theory of electroplating

The electroplating bath consists of the anode, cathode and an electrolytic solution. The metal salt in the aqueous solution undergoes ionisation, and under the influence of potential difference the cations migrate to the cathode and get deposited on it. These ions are continuously replenished by the dissociation of the anode. For example, if zinc is to be deposited on iron then the cathode is made of iron and the anode is made up of zinc. The electrolytic solution is ZnSO_4 , which ionises to form Zn^{2+} ions and SO_4^{2-} ions. The zinc ions migrate to the cathode and get deposited at the cathode and the SO_4^{2-} ions migrate to the anode and combines with zinc metal of the anode to form zinc sulphate. This zinc sulphate then dissolves in the electrolyte and maintains its concentration.



If the anode is made of inert material like graphite then electrolytic salt is added continuously to the electroplating bath to maintain the concentration of the electrolyte.

Factors affecting the nature of deposit are as follows

- Current density** The quantity of the metal deposited at the cathode is guided by the Faradays law of electrolysis, according to which the amount of substance deposited or dissolved at any electrode is directly proportional to the quantity of electricity passing through the electrolyte. The thickness of the metal deposited by electroplating depends upon the current density, which is defined as the current per unit surface area of the cathode. It is expressed in terms of A m^{-2} or mA cm^{-2} .

Current density increases on increasing the applied voltage and reaches a limiting value. During electroplating, current density should be optimum for proper deposit. If the current density is low, the surface diffusion is faster than electron transfer and hence the atoms find favorable sites and deposit uniformly on the metal surface. As the current density increases, the rate of electron transfer rises, whereas the rate of surface transfer retards. At high current density below the limiting value, the deposit becomes loose as well as brittle. The upper limit of current density in electroplating can be increased by maintaining the electrolyte at elevated temperature and also by stirring it.

At very high current density above the limiting value, the evolution of hydrogen on the surface predominates, causing depletion of H^+ ions in the vicinity of the cathode. This leads to the formation of dispersed deposits containing metal oxides and hydroxides.

- Various additives improve the quality of the deposit.
- Strong, adherent and smooth deposits can be obtained by adding various additives like boric acid, urea, glycine, gelatin and glue in minute quantities (about 0.1%) to the electrolyte bath. In the absence of these additives, the deposit is rough, granular and mechanically weak.
- *Complexing agents* form metal ion complexes and help in obtaining fine grained and more adherent deposits. Presence of CN^- ions help in obtaining smooth and adherent deposits of Cu, Ag, Au, Cd, Zn, etc.
- *Brighteners* Organic additives like aromatic sulphonates or sulphones and compounds containing $C\equiv N$, $C=O$ or $-N=C=S$ groups like coumarin and thiourea help in producing 'microscopic fine deposits' that reflect the light falling on the surface and increases the brightness of the deposit. Similarly, additives like sodium formate and cobalt sulphate are added as brighteners for nickel deposit.
- *Levellers* These substances help to produce uniform deposits on the metal surface. Sodium allylsulphate is used as a leveller for nickel plating. These compounds perform the twin function of levelling and improving brightness.
- *Structure modifiers* Also called stress relievers, they help in modifying the structure of the electrodeposit. Saccharin is employed as a common stress reliever to relieve the internal stress of the deposit and prevent it from dislodging under the effect of any impact.
- *Wetting agents* These agents help to release hydrogen gas bubbles from the surface of the cathode. In the absence of these agents, the gas bubbles get trapped and try to escape after the electroplating making it brittle. Sodium lauryl sulphate, a synthetic detergent, is the commonly used wetting agent.
- *pH* Proper pH should be maintained to get a good electrodeposit. The pH of the electrolytic bath is generally kept between 4 (moderately acidic) to 8 (slightly alkaline). Nickel plating is carried out at pH 5.5–5.7 (acidic medium) by adding boric acid as a buffer.

The pH lower than the optimum range leads to hydrogen evolution at the cathode, resulting in a burnt deposit, and pH higher than the optimum range leads to the precipitation of metal hydroxides on the electrode surface.

Requirements of the electrolyte (depositing solution)

The electrolytic solution used for the electrolytic bath should satisfy the following requirements

- Its conductivity should be high. The conductivity of the electrolytic solution can be increased by adding compounds like sulphuric acid.
- It should be highly soluble, its metal content should be high and the metal ions should not precipitate simply by immersion of the metal.
- It should be stable and should not undergo hydrolysis, oxidation, reduction or other chemical changes.

- The solution should dissolve the anode effectively and should be capable of maintaining a constant metal content in the solution.
- The electrolyte should have good *throwing power* and should be able to give a uniform deposit even on irregular surface.

(Throwing power can be defined as the ability of the electrolyte cell to discharge metal ions on the cathode to give a uniform deposit. It is calculated as the ratio of thickness of the deposit in a hole to the deposit on the surface during the same time and conditions).

No single electrolyte fulfills all the above-mentioned requirements, hence various additives are added to the electrolytic solution according to the requirement.

Electroplating of some metals

1. **Nickel plating** For nickel plating, generally iron is used as the base metal. As nickel is cathodic to iron hence, the coating should be thick and nonporous as corrosion of iron may occur at the pin holes making the surface rusty. A thin copper coating is applied between the two coatings of nickel so that the pores can be removed. The anode consists of nickel pellets or pieces in a titanium mesh baskets, and the cathode is made of the material to be electroplated. Two types of electrolytic baths can be used for nickel plating

- (a) **Sulphate bath** The composition per liter of the bath solution is 250 g nickel sulphate, 45 g nickel chloride, 30 g boric acid and rest water. The bath containing this solution is operated at a temperature of 40 °C–70 °C, at a pH of 4.5–4.7. The current density is 20–50 mA/cm². Additives like coumarin, saccharin and benzene sulphonamide are added to the electrolytic bath to improve the quality of the coating. If a hard deposit is required, then nickel sulphate is replaced by nickel ammonium sulphate.

The coating thus obtained finds application as an undercoat for chromium plating.

- (b) **Sulphamate bath** The composition per liter of the bath solution is 600 g nickel sulphamate, 5 g nickel chloride, 40 g boric acid and rest water. The operating temperature of the bath is 50 °C–60 °C at a pH of about 4. The current density is 50–60 mA/cm². The additive in this case is naphthalene 1, 3, 6-trisulphonic acid.

This bath finds use in electroplating for decorative purposes for obtaining mirror finish of the electroplated article.

2. **Copper plating** For copper plating, the anode is made of copper and the cathode is the material to be electroplated. The electrolytic bath may be acidic or alkaline.

- (a) **Acidic bath** Also called sulphate bath, it consists of 200–250 g/L CuSO₄, 50–75 g/L H₂SO₄ and rest water. The additives are gelatin or dextrin, sulphur-containing brightener and sulphonc acid. The operating temperature is 20 °C–40 °C. The pH is low and the current density is about 20–50 mA/cm².

This bath is used for coating in printed circuit boards (PCB) and is not suitable for electroplating iron and its alloys.

- (b) **Alkaline bath** It is also called cyanide bath. The composition per liter of the bath is as follows: CuCN: 40–50 g, KCN: 20–30 g, 10 g K₂CO₃ and rest water. Brighteners

like Al_2O_3 and thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) are also added to the electrolytic bath. The pH is maintained between 12 and 13, current density used is $10\text{--}40\text{ mA/cm}^2$ and the temperature of the bath is $40\text{--}50\text{ }^\circ\text{C}$.

This bath finds application in the coating of printed circuit boards and is also suitable for plating iron and its alloys. It is used as an undercoating for chromium plating.

3. **Chromium plating** Chromium plating is generally thin with numerous pores. The number of pores increases as the thickness of the coating increases so that the coating has a tendency to crack. Therefore, chromium plating is always done on copper or nickel undercoat.

The anode is made of Pb–Sn or Pb–Sb alloy coated with PbO_2 (or stainless steel) and cathode is made up of the material to be electroplated. The electrolytic bath is prepared by dissolving 250 g chromic acid, 25 g of sulphuric acid (100:1) per dm^3 and 1 g of trivalent chromium (Cr^{3+}). The temperature is $45\text{--}55\text{ }^\circ\text{C}$ and the current density is $100\text{--}200\text{ mA cm}^{-2}$.

Chromium plating produces a hard, corrosion-resistant film with an attractive appearance and brightness. It is used extensively in automobile industry, household fittings, surgical instruments, sanitary fittings, tools used for cutting, polishing, cylinder linings, piston rings, optical instruments, machine parts, solar energy collectors, etc.

4. **Gold plating** It is the electrodeposition of gold on other metals. As gold is a noble metal, it does not have the tendency to lose electrons and get oxidized. Under such a situation if gold is plated on copper, brass or bronze, the metal ions from these metals will diffuse into the gold layer and reduce hardness. In order to avoid this, a layer of nickel is first coated as a barrier metal. Both nickel and gold are deposited by electroplating to get a sandwich of copper-nickel-gold. The electrolytic baths used for gold plating may be **cyanide-based plating baths** and **non-cyanide plating baths**.

The **cyanide plating baths** are further of three types

- (i) *Alkaline gold cyanide bath* with pH > 8.5. It contains 8–20 g/L of potassium gold cyanide and 15–100 g/L of potassium cyanide. The current density is $11\text{--}86\text{ A m}^{-2}$. It is used for gold and gold alloy plating.
- (ii) *Acidic-buffered baths* with pH between 1.8 and 6. It contains potassium gold cyanide $\text{KAu}(\text{CN})_2$ 8 to 16 g/L, citric acid 90–115 g/L, cobalt (added as acetate or sulphate) 0.07–0.1 g/L. The pH of the bath is adjusted with KOH and the temperature is maintained at $40\text{--}65\text{ }^\circ\text{C}$. It is used for bright hard gold and gold alloy plating.
- (iii) *Neutral gold cyanide bath* with pH between 6 and 8.5. It contains $\text{KAu}(\text{CN})_2$ 8–30 g/L, KH_2PO_4 100 g/L. The pH is adjusted with the help of KOH and the temperature range is $25\text{--}45\text{ }^\circ\text{C}$. It finds use in high-purity gold plating.

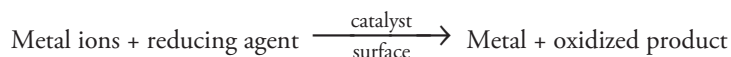
Non-cyanide baths These are generally sulphite- or chloride-based baths. The sulphite baths generally use Au (I) sulphite but the complex is susceptible to disproportionation and forms Au (III) and metallic gold. Therefore, mixed thiosulphate and sulphite electrolytes are used. They produce soft gold deposits that are used in electronic devices and on IC's. The pH is maintained to 6 and working temperature is around $60\text{ }^\circ\text{C}$. Apart from this, sulphide-thiosulphate baths are also used to produce soft gold deposits for wire-bonding applications. In this bath, the pH is maintained to 5 and the temperature is kept at $50\text{ }^\circ\text{C}$.

Applications

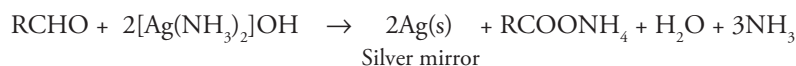
Gold plating finds extensive use in jewellery, in electronic industry, in the integration of electronic circuits, PCBs and in semiconductor industry.

3.11 Electroless Plating

In electroless plating, a noble metal (less reactive metal) is deposited on a less noble metal (more reactive metal) without the passage of electric current. It involves a redox reaction catalysed by the metal of the alloy being deposited; hence, it is also termed as autocatalytic coating. The method employs a suitable reducing agent to bring about the reduction of metal ions to metal that gets deposited over catalytically active surface.



This technique has been used for manufacturing mirrors by the reduction of a complexed metal with the help of a mild reducing agent like formaldehyde.



A shining coating of elemental silver deposits on the metal surface.

Advantages of electroless plating

1. Electrical energy is not used.
2. It helps in coating nonconducting objects, nonmetallic surfaces like plastics, semiconductors.
3. The throwing power is unlimited.
4. No excess deposit at joints.
5. Edges, inside holes, irregular objects and objects of complex geometries and shapes can easily be coated evenly. It is difficult to coat these surfaces by electroplating.
6. Hydrogen gas is not trapped in the blind holes.
7. Resulting deposits have unique physical, chemical, mechanical and magnetic properties.
8. Coating is harder and less porous than regular coating.
9. The use of levellers is eliminated.

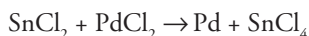
Disadvantages of electroless plating

1. Process is expensive as the chemicals used cost high.
2. Rate of deposition is rather slow.
3. A careful analytical control of the bath is required.

Electroless plating process

1. **Preparation of active surface of the metal to be electroplated** First the surface is treated chemically to remove oils and other corrosive elements. This is followed by surface activation employing any one of the following methods

- Surface may be subjected to etching by acid treatment.
- The surface may be electroplated with a thin layer of the metal to be plated or any other suitable metal. This is followed by heat treatment.
- Plastics and printed circuit boards are activated by treating with stannous chloride followed by dipping in palladium chloride solution. As a result of this treatment a thin layer of Pd deposits on the surface that serves as catalytic surface on plastic.



2. **Electroless plating bath** The electroless plating bath consists of the following
 - Chloride, sulphate or any other soluble salt of the metal to be plated.
 - Reducing agents like formaldehyde, sodium hypophosphite, etc.
 - Complexing agents like tartarates, citrates, succinates, EDTA.
 - Accelerators or exaltants like succinates, glycinate and fluorides to enhance the rate of plating.
 - Stabilisers like thiourea, cations of lead, calcium, thallium to prevent the decomposition of the plating bath solution.
 - Buffers like sodium acetate, boric acid, sodium hydroxide and Rochelle salt to control the pH of the bath.

Electroless plating of some metals

1. **Nickel** Oil, grease and other impurities are removed chemically from the surface to be plated. Different surfaces are activated as summarized in Table 3.7.

Table 3.7 Metal surfaces and chemicals used for activation.

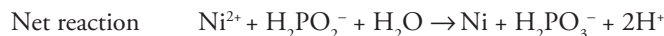
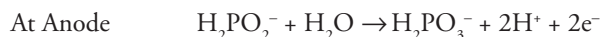
Surface to be plated	Chemical used for activation
Al, Cu, Fe, brass, Au, Ag, Pt, Rh and Co	No activation required and nickel is plated directly on their surface
Stainless steel	By dipping in hot solution of 50% dilute H_2SO_4
Magnesium alloy	Thin coating of Zn and Cu over it
Nonmetallic articles like plastics, glass or quartz	They are first dipped in SnCl_2 solution containing HCl followed by dipping in palladium chloride so that a thin activating surface layer of Pd is formed on their surface

Bath The coating bath contains the following

- Coating solution – 20 g/L of NiCl_2
- Reducing agent – 20 g/L of sodium hypophosphite
- Complexing agents cum exhaltant – 15 g/L sodium succinate
- Buffer – 10 g/L of sodium acetate.

The pH of the bath is maintained at 4.5 and temperature is 93 °C.

Following reactions take place when the activated surface is dipped in the bath



As seen above H^+ ions are liberated in the reaction hence the pH of the bath goes down which adversely affects the quality of the plating. Consequently continuous addition of the buffer is essential to maintain the pH. NiCl_2 and hypophosphite are also consumed and need to be replenished continuously. In addition to the above reactions there may be formation of phosphorus which results in Ni- P alloy deposition.

Applications

1. Owing to excellent throwing power, this method is applied for coating objects with complex geometrical shapes and also on the internal diameter of tubular parts that are otherwise difficult to access.
2. It is used for plating several components like pistons, fasteners, pipes, valves, shafts and hydraulic systems, fuel injection assemblies.
3. Electroless nickel plating finds use in jewellery, electroless nickel plating on acrylonitrile butadiene styrene polymer (ABS) is used in decorative items.
4. In electrical industry electroless Ni-P coating is used in making magnetic components.

Electroless plating of copper

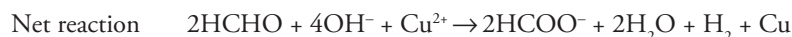
Surface preparation is followed by dipping the metal in the plating bath. The metal surface to be coated is degreased chemically and etched (treated with acid) if required. Au, Ag, Pt, Rh, Co and Fe surfaces do not require activation and are plated directly. Insulators like glass, plastics, printed circuit boards PCBs are activated by dipping in SnCl_2 solution containing HCl followed by dipping in palladium chloride solution so that a thin layer of palladium deposits on the surface.

Bath It consists of the following

- Coating solution – 12 g/L CuSO_4
- Reducing agent – 8 g/L HCHO

- Buffer – 15 g/L NaOH + 14 g/L Rochelle salt
- Complexing agents cum exhaltant – 20 g/L EDTA

The pH is maintained at 11–12 and the optimum temperature of the bath is 25 °C. The following reactions are involved



OH^- ions are consumed in the reaction reducing the pH of the bath, which is maintained by the continuous addition of buffer. CuSO_4 and HCHO are also used in the reaction and are replenished continuously.

Applications

Plating through holes in case of double-sided and multilayered printed circuit boards (PCBs) are effectively carried out by the electroless plating techniques only.

Summary

- Corrosion is the process of destruction or deterioration of metals by direct (chemical) or indirect (electrochemical) attack with the environment.
- Dry or chemical corrosion occurs by the direct chemical action of the environment with the metal surface in the absence of moisture. Direct reaction of metal surface with oxygen of the environment is called oxidation corrosion.
- The rate and extent of oxidation corrosion depends upon the nature of the oxide film, which can be stable, unstable, volatile and porous.
- The extent of protection given by the oxide film to the underlying metal is governed by the “Pilling–Bedworth Rule”, which states that if the volume of the oxide film is *less* than the volume of metal then the oxide layer is porous and hence nonprotective and if the volume is *equal to* or *greater than* the volume of the metal the oxide film is continuous, nonporous and protective, that is, further corrosion does not take place.
- Electrochemical corrosion or indirect corrosion occurs due to the formation of electrochemical cells on the metal surface.
- Formation of electrochemical cells requires
 - (1) Separate anodic and cathodic areas
 - (2) Presence of an electrolyte.

- In electrochemical corrosion oxidation occurs at the anode and the anodic metal undergoes corrosion. The reaction at the cathode depends on the environment. The corrosion product is formed closer to the cathode.
- Galvanic corrosion is a type of electrochemical corrosion in which two metals of different reactivities are in direct contact in the presence of an electrolyte. The more reactive metal is anodic and undergoes corrosion.
- When a metal is in contact with an electrolyte of varying concentrations or varying aeration, it leads to the formation of concentration cell and is called concentration cell corrosion. For example, caustic embrittlement where iron in contact with different concentrations of NaOH undergoes corrosion.
- A metal in contact with different concentrations of oxygen leads to the formation of electrochemical cell and this is called differential aeration corrosion. It is an example of concentration cell corrosion. Areas deficient in oxygen behave as anode and oxygen rich areas become cathodic .
- Examples of differential aeration corrosion are
 - (i) Pitting corrosion
 - (ii) Waterline corrosion
 - (iii) Stress corrosion
 - (iv) Corrosion under a drop of water, leaf, stone, block of wood, etc.
 - (v) Crevice corrosion
 - (iv) Intergranular corrosion, etc.
- Galvanic series gives us a real and useful picture about the corrosion tendency of a metal. The position of a metal in galvanic series may vary depending on the environment.
- The rate and extent of corrosion depends on
 - (i) Nature of the metal : Relative areas of anodic and cathodic parts, purity of the metal, physical state of metal, nature of the surface film and solubility of the corrosion products.
 - (ii) Nature of the corroding environment : Factors like temperature, humidity in air, presence of impurities, pH, etc.
- Corrosion control : Corrosion can be controlled in a number of ways like proper designing, use of pure metal and corrosion-resistant alloys, modifying the environment (removing air, humidity, acids from the environment), modifying the properties of the metal by alloying and refining and by using inhibitors.
- Electrochemical protection of corrosion

Cathodic protection : The metal to be protected is made a cathode either by connecting it to a more reactive metal (sacrificial anode cathodic protection) or by connecting it to the cathode of a DC battery (impressed current cathodic protection).

- **Metallic coating :** They are of two types
 - Anodic coating : Coating of a more reactive metal on the base metal. For example, coating of Zn on Fe.
 - Cathodic coatings : Coating of less reactive metal on the base metal. For example coating of tin on iron.
- Metallic coatings can be applied by various methods like hot dipping (galvanising and tinning), electroplating, metal cladding and spraying.
- Nonmetallic coatings can be organic coatings like paints, varnishes, lacquers, enamels, etc and inorganic like phosphate coating and chromate coating.
- Electroplating is done in two steps : The first step is surface preparation, which is done by mechanical cleaning, solvent cleaning, alkali cleaning, pickling and etching, sand blasting, etc.
 - The second step is electrodeposition where the metal to be coated is made anode and the base metal is made cathode and the two are dipped in a suitable electrolytic solution.
- Electroless plating is the plating of a noble metal on a reactive metal in the presence of a reducing agent without the use of electric current.

Review Questions

1. Define corrosion. Why do metals corrode and what are the consequences of corrosion?
2. What do you mean by 'dry corrosion' or 'chemical corrosion'? Explain the mechanism with the help of a well-labeled diagram.
3. Explain the 'Pilling–Bedworth rule'.
4. Explain the mechanism of 'wet corrosion or electrochemical corrosion'.
5. What is the difference between chemical corrosion and electrochemical corrosion.
6. Explain the following
 - (i) Pitting corrosion
 - (ii) Stress corrosion
 - (iii) Galvanic corrosion
 - (iv) Caustic embrittlement
 - (v) Concentration cell corrosion
 - (vi) Differential aeration corrosion
 - (vii) Intergranular corrosion
 - (viii) Waterline corrosion
 - (ix) Galvanic series
 - (x) Passivation

7. Explain in detail the various factors affecting corrosion.
8. Discuss sacrificial anode cathodic protection. What is the condition for a metal to act as a sacrificial anode?
9. What is cathodic protection? Explain.
10. Explain impressed current cathodic protection method to prevent corrosion.
11. 'Design of equipment plays a significant role in controlling corrosion'. Justify the statement.
12. How can you control corrosion by modifying the environment or modifying the properties of the metal?
13. What are protective coatings? How are anodic coatings better than cathodic coatings?
14. What is galvanisation and tinning? Explain.
15. Write short notes on the following
 - (i) Hot dipping
 - (ii) Electroplating
 - (iii) Metal cladding
 - (iv) Organic coatings
 - (v) Inorganic coatings.
16. What is electroplating? Explain the process of electroplating in detail.
17. What is electroless plating? Differentiate between electroplating and electroless plating and explain the advantages of electroless plating.
18. Explain the process of electroplating of the following metals
 - (i) Nickel plating
 - (ii) Copper plating
 - (iii) Chromium plating
 - (iv) Gold plating
20. What do you understand by electroless plating? Explain the process of electroless plating of nickel.
21. Explain the various methods of surface preparation prior to electroplating.

Multiple Choice Questions

1. Metal and their alloys corrode in nature because
 - (a) Metals are unstable
 - (b) Metals have a tendency to go back to their original form of occurrence
 - (c) In nature metals are at low energy
 - (d) Corrosion leads to the formation of stable corrosion products

2. The corrosion of metals due to direct chemical attack of the environment on the metal surface in the absence of moisture is
 - (a) Dry corrosion
 - (b) Chemical corrosion
 - (c) Both the above
 - (d) Electrochemical corrosion
3. Which of the following metal forms a volatile oxide film leading to rapid and continuous corrosion
 - (a) Molybdenum
 - (b) Aluminium
 - (c) Platinum
 - (d) Lead
4. The metal that does not form a fine grained tightly sticking impervious corrosion product
 - (a) Aluminium
 - (b) Tin
 - (c) Lead
 - (d) Silver
5. According to Pilling – Bedworth rule a metal undergoes continuous corrosion if the volume of the oxide film formed is
 - (a) Greater than the volume of the metal underneath
 - (b) Equal to the volume of the underlying metal
 - (c) Less than the volume of the metal lying underneath
 - (d) None of the above
6. According to the wet or electrochemical theory, corrosion occurs at the
 - (a) Cathode
 - (b) Anode
 - (c) Both anode and cathode
 - (d) In between the anode and cathode
7. According to the wet or electrochemical theory of corrosion, the corrosion product is formed
 - (a) At the anode
 - (b) At the cathode
 - (c) Near the cathode
 - (d) Exactly between anode and cathode
8. Which of the following is an example of differential metallic corrosion or bimetallic corrosion
 - (a) Galvanic corrosion
 - (b) Stress corrosion
 - (c) Waterline corrosion
 - (d) Caustic embrittlement
9. Which of the following is not an example of differential aeration corrosion
 - (a) Pitting corrosion
 - (b) Waterline corrosion
 - (c) Stress corrosion
 - (d) Galvanic corrosion
10. The rate of corrosion is high if
 - (a) Anodic areas are small and cathodic areas are large
 - (b) Anodic areas are large and cathodic areas are small
 - (c) Both anodic and cathodic areas are large
 - (d) Does not depend upon the area of anode and cathode
11. Iron will not corrode if the pH is above
 - (a) 2
 - (b) 7
 - (c) 6.5
 - (d) 10

12. Corrosion can be prevented by
 - (a) Connecting the base metal to a more reactive metal
 - (b) Connecting the base metal to the cathode of a DC battery
 - (c) Coating the base metal with zinc or tin coating
 - (d) All of the above
13. Galvanisation is the process of
 - (a) Coating Zn on Fe
 - (b) Coating Sn on Fe
 - (c) Coating Zn on Cu
 - (d) Coating Mg on Fe
14. Iron articles are galvanized by
 - (a) Electroplating
 - (b) Spraying molten zinc on iron
 - (c) Hot dipping
 - (d) All the above
15. The process of depositing a noble metal on a less noble metal in the presence of a reducing agent without the use of electric current is
 - (a) Electroplating
 - (b) Electroless plating
 - (c) Electrical plating
 - (d) None of the above
16. In electroplating, the metal to be coated or electroplated is made
 - (a) Anode
 - (b) Cathode
 - (c) Either anode or cathode
 - (d) Neither anode nor cathode
17. Which of the following is not a technique for surface preparation
 - (a) Solvent cleaning
 - (b) Pickling and etching
 - (c) Spraying
 - (d) Mechanical cleaning
18. Acid pickling is not used for the surface preparation of
 - (a) Nickel
 - (b) Aluminium
 - (c) Steel
 - (d) Brass
19. Brighteners are added to the plating bath to
 - (a) Have uniform deposit
 - (b) Increase the brightness of the deposit
 - (c) Increase the throwing power
 - (d) Make the deposit smooth, strong and adherent
20. The optimum temperature and pH for nickel plating is
 - (a) 40-70 °C and pH 4 to 5 respectively
 - (b) 40-60 °C and pH 3 to 4 respectively
 - (c) 20-40 °C and pH 5 to 7 respectively
 - (d) 60-70 °C and pH 6 to 8 respectively
21. The advantage of electroless plating over electroplating is that in electroless plating
 - (a) No electrical energy is used
 - (b) Nonconductive surface like plastics can be coated
 - (c) No excess deposits at the joints
 - (d) All of the above

22. The buffer used to maintain pH 11–12 in electroless plating of copper is
- (a) Sodium acetate
 - (b) Ammonium chloride + ammonium hydroxide
 - (c) Sodium hydroxide + Rochelle salt
 - (d) Acetic acid and sodium acetate

Solutions

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (c) | 3 (a) | 4 (d) | 5 (c) | 6 (b) | 7 (c) | 8 (a) |
| 9 (d) | 10 (a) | 11 (d) | 12 (d) | 13 (a) | 14 (c) | 15 (b) | 16 (b) |
| 17 (c) | 18 (b) | 19 (b) | 20 (a) | 21 (d) | 22 (c) | | |

Chapter 4

PHASE RULE

4.1 Introduction

The phase rule was given by Gibbs, which explains the equilibrium existing in heterogeneous systems. It states that the equilibrium between different phases is influenced by temperature, pressure and concentration only and not gravity, electrical or magnetic forces. The number of degrees of freedom (F), which will be explained later, is related to the number of components (C) and phases (P) by the following phase rule equation.

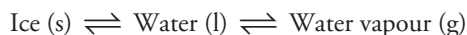
$$F = C - P + 2$$

4.2 Explanation of Terms

Phase A phase is a homogenous, physically distinct and mechanically separable portion of a system which is separated from other parts of the system by a definite boundary.

Examples

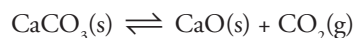
1. A gaseous mixture, being thoroughly miscible in all proportions constitutes one phase only.
2. If two liquids are immiscible (e.g., oil and water), they will constitute two separate phases.
3. Two miscible liquids (e.g., water and alcohol) constitute one phase only.
4. A solute completely dissolved in a solvent constitutes a *single* phase, for example, a solution of glucose in water, salt in water, etc.
5. At freezing point, water consists of *three* phases.



6. Each solid constitutes a separate phase. A mixture of rhombic and monoclinic sulphur is a *two* phase system.

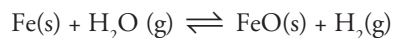
A solid solution irrespective of the number of solids present is a *single* phase system.

Calcium carbonate decomposes as follows:



The above equilibrium has *three* phases (two solid and one gaseous)

Similarly,



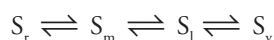
Here there are two solid phases, Fe and FeO and one gaseous phase consisting of $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$. Hence, there are *three* phases in equilibrium.

7. A homogenous solution of Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ constitutes a single phase.

Components The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation. While expressing the composition of a phase in terms of its components, zero and negative quantities are permissible. The components of a system do not represent the number of constituents or chemical individuals present in the system.

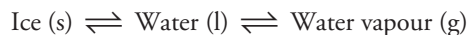
For example

- (i) The sulphur system consists of four phases – rhombic, monoclinic, liquid and vapour.



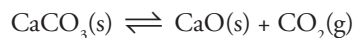
The composition of each phase can be expressed in terms of sulphur alone. Hence, it is a one-component system.

- (ii) Water system has three phases.



Each of these phases is a different physical form of the same chemical compound represented by H_2O . Hence, it is a one-component system.

- (iii) The thermal decomposition of calcium carbonate involves three phases.



However, the composition of each of these three phases can be expressed in terms of at least two constituents. Hence it is a two-component system.

When CaO and CO_2 are considered as components:

Phase	Components
CaCO_3	$\text{CaO} + \text{CO}_2$
CaO	$\text{CaO} + 0\text{CO}_2$
CO_2	$\text{CO}_2 + 0\text{CaO}$

(iv) The thermal decomposition of MgCO_3 is as follows:



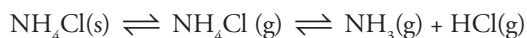
This is also a two-component system as the composition of each of the three phases can be expressed in terms of two constituents.

For example,

When MgO and CO_2 are considered as components

Phase	Components
MgCO_3	$\text{MgO} + \text{CO}_2$
MgO	$\text{MgO} + 0\text{CO}_2$
CO_2	$\text{CO}_2 + 0\text{MgO}$

(v) In the dissociation of NH_4Cl in a closed vessel, the following equilibrium occurs.



The system consists of two phases, viz., solid NH_4Cl and homogenous gaseous mixture consisting of NH_3 and HCl . An equimolar mixture of NH_3 and HCl in the vapour phase may be regarded as NH_4Cl in the vapour state, and hence it is a one-component system.

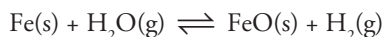
Addition of NH_3 or HCl to the system makes it a two-component system because the composition of the vapour phase can no longer be described by NH_4Cl alone.

Phase	Component
$\text{NH}_4\text{Cl}(\text{s})$	NH_4Cl
$\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ Equivalent quantity	$\text{NH}_4\text{Cl}(\text{g})$
$\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ Excess NH_3	$\text{NH}_4\text{Cl}(\text{g}) + \text{NH}_3(\text{g})$
$\text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ Excess HCl	$\text{NH}_4\text{Cl}(\text{g}) + \text{HCl}(\text{g})$

(vi) In a system of sodium sulphate and water, various phases may exist like Na_2SO_4 ; $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$; ice, solution and vapour. The composition of each phase can be expressed in terms of Na_2SO_4 and H_2O . Hence the system is a two-component system.

Phase	Component
$\text{Na}_2\text{SO}_4(\text{s})$	$\text{Na}_2\text{SO}_4 + 0\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$
Na_2SO_4 solution	$\text{Na}_2\text{SO}_4 + x\text{H}_2\text{O}$

(vii) In equilibrium,



The minimum number of components required to express the composition is three, and hence it is a three-component system.

(viii) $\text{PCl}_5(\text{s}) \rightleftharpoons \text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g})$

At lower temperature, the system has three phases but the number of components is only two. At higher temperature, only the gaseous phase exists; hence, it will be a one-component system.

(ix) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{CuSO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{g})$

It is a two-component system.

(x) An aqueous solution of NaCl is a two-component system. The constituents are NaCl and H_2O and both are necessary to describe the composition of the solution phase.

The unsaturated solution of NaCl in water is a two-phase and two-component systems, whereas saturated solution of NaCl in water is a three-phase and two-component systems.

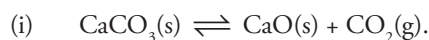
Degrees of freedom

The number of degrees of freedom of a system is the minimum number of independent variables of a system, such as temperature, pressure and concentration which can define a system in equilibrium completely. Let us consider some examples:

1. In a water system when all the three phases, ice, water and water vapour, are in equilibrium $\text{ice} \rightleftharpoons \text{water} \rightleftharpoons \text{water vapour}$, the degree of freedom is zero and the system is said to be invariant or non-variant. This is because the three phases coexist at the freezing point of water where the temperature and pressure are automatically fixed and there is no need to specify any variable.
2. When $\text{water} \rightleftharpoons \text{water vapour}$, the degree of freedom is one and the system is univariant. Only one variable, either temperature or pressure is to be specified to define the position of the system because on specifying one variable the other automatically becomes fixed.
3. For a system containing pure gas or only one phase, both temperature and pressure have to be defined to specify the position of the system. Hence the system is bivariant and the degree of freedom is two.

Problems

(1) Calculate the number of phases present in the following systems:



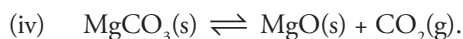
Three (two solid and one gaseous phase)

(ii) A system consisting of benzene and water.

As the two liquids are immiscible, there will be two phases – benzene and water.

(iii) A gaseous mixture of N_2 , H_2 and NH_3 .

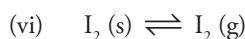
One (a gaseous mixture is a homogenous mixture)



Three

(v) Rhombic sulphur(s) \rightleftharpoons Monoclinic sulphur(s).

Two



Two

(vii) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ equimolar amount.

Two

(viii) $\text{Ice}(\text{s}) \rightleftharpoons \text{Water}(\text{l}) \rightleftharpoons \text{Water vapour}(\text{g})$

Three

(ix) An emulsion of oil in water.

Two

(x) Closed beaker partially filled with benzene and water.

Three (benzene, water and vapours)

(xi) Acetone and water.

Two (since acetone and water are miscible, the two phases are liquid + vapour)

(xii) A saturated solution of NaCl.

Three (solid NaCl + solution + vapour; unsaturated solution of NaCl in water is a two phase two-component system, whereas a saturated solution of NaCl in water is a three phase two-component system)

(xiii) Mixture of O_2 and N_2

One

(xiv) Finely ground mixture of graphite, sulphur and sodium chloride.

Three

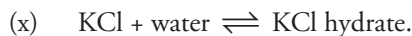
(xv) A mixture of diamond powder and graphite.

Two

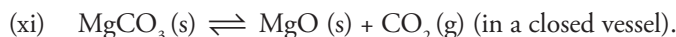
- (xvi) Aqueous solution saturated with KCl and NaCl in contact with solid NaCl.
Two (solid NaCl + solution of KCl and NaCl)
- (xvii) An iceberg floating on clear sea water in the presence of clean air.
Three (solid iceberg + liquid sea water + clean air)
- (xviii) $\text{Fe(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{FeO(s)} + \text{H}_2\text{(g)}$ equilibria.
Three (Two solid phases, Fe(s) and FeO(s) and one gaseous phase consisting of $\text{H}_2\text{O(g)}$ and $\text{H}_2\text{(g)}$)
- (xix) Solution of Mohr's salt $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$.
One phase (as it forms a homogenous mixture with water and the crystals of FeSO_4 and $(\text{NH}_4)_2\text{SO}_4$ are not physically distinct).

2. Calculate the number of components present in the following systems.

- (i) $\text{CaCO}_3\text{(s)} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$.
Two
- (ii) $\text{Ag(s)} + \text{Ag-Pb solution(l)} + \text{Pb(s)} + \text{Ag vapour(g)}$.
Two (Ag and Pb)
- (iii) $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)}$.
One (As $\text{H}_2\text{(g)} + 1/2 \text{O}_2\text{(g)} = \text{H}_2\text{O(g)}$)
- (iv) $\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{(g)} + \text{H}_2\text{O(g)}$.
Two (H_2O and H_2)
- (v) $\text{NH}_4\text{Cl(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{HCl(g)}$.
One (As $\text{NH}_3\text{(g)} + \text{HCl(g)} = \text{NH}_4\text{Cl(g)}$ when NH_3 and HCl are in equimolar ratio)
- (vi) $\text{NH}_4\text{Cl(s)} \rightleftharpoons x\text{NH}_3\text{(g)} + y\text{HCl(g)}$.
Two ($\text{NH}_4\text{Cl(s)}$ and either $\text{NH}_3\text{(g)}$ or HCl(g) whichever is in excess)
- (vii) $\text{NaCl(s)} \rightleftharpoons \text{NaCl(aq)}$ or a solution of common salt.
Two (NaCl and water)
- (viii) When ammonia dissociates in (a) a closed vessel (b) a closed vessel containing nitrogen.
(a) One (only NH_3) (b) Two (NH_3 and N_2)
- (ix) $\text{Water} \rightleftharpoons \text{Water vapour}$.
One



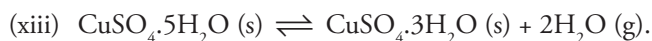
Two



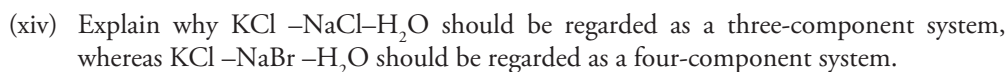
Two



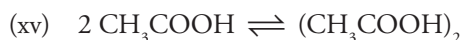
Three



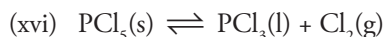
Two (because the composition of each phase can be expressed with the help of two-components CuSO_4 and H_2O)



A system of KCl , NaCl and H_2O is a three-component system because the composition of all five phases, solid NaCl , solid KCl , solid H_2O , solution and vapour can be expressed in terms of three species— NaCl , KCl and H_2O . A system consisting of KCl , NaBr and H_2O is a four-component system (note the difference between the two systems—the first one has two salts with a common chloride ion).

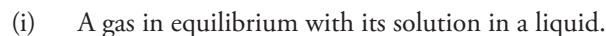


One



The number of phases is three, but the number of components is two. The above system is a two-component system at lower temperatures but at higher temperatures, all the three constituents, viz., PCl_5 , PCl_3 and Cl_2 will be in gaseous state, and under these conditions, it will be a one-component system.

3. Calculate the degree of freedom in the following systems:



$$F = C - P + 2$$

Components = 2 (gas + liquid); phases = 2 (gas + liquid)

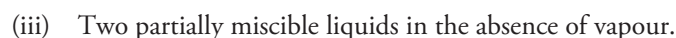
$$F = 2 - 2 + 2 = 2$$



$$F = C - P + 2$$

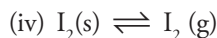
Components = 2 (solid + liquid); phases = 2 (solution of solid in liquid + vapour)

$$F = 2 - 2 + 2 = 2$$



Phases and components = 2 (two miscible liquids)

$$F = C - P + 2; F = 2 - 2 + 2 = 2$$



$$C = 1; P = 2$$

$$F = C - P + 2; F = 1 - 2 + 2 = 1$$



$$C = 1; P = 1$$

$$F = C - P + 2; F = 1 - 1 + 2 = 2$$

4. If $NH_4Cl(s)$ is allowed to dissociate in a vessel already containing some $NH_3(g)$, what is the value of the degree of freedom.

$$F = C - P + 2$$

$$C = 2 (NH_4Cl + NH_3); P = 2 [NH_4Cl(s) + \{NH_4Cl(g) \& NH_3(g)\}]$$

$$F = 2 - 2 + 2 = 2$$

5. With the help of phase rule, calculate the degree of freedom of the following system.

- (a) Ice and water in equilibrium

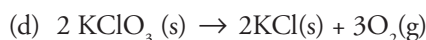
$$P = 2; C = 1; F = C - P + 2; F = 1 - 2 + 2 = 1$$

- (b) Silver and lead at the eutectic point

$$C = 2, P = 3; F = C - P + 1 (\text{condensed phase rule}); F = 2 - 3 + 1 = 0$$

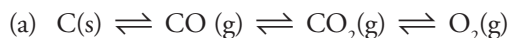
- (c) Saturated solution of NaCl

$$C = 2, P = 2; F = C - P + 2; F = 2 - 2 + 2 = 2$$



$$P = 3, C = 2; F = C - P + 2; F = 2 - 3 + 2 = 1$$

6. Calculate the number of phases, components and degree of freedom of the following systems.



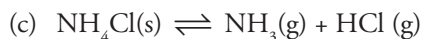
Phases = 2 (solid phase due to carbon + gaseous phase due to $CO_2 + CO + O_2$)

$$C = 2 (\text{carbon} + \text{oxygen})$$

$$F = C - P + 2; 2 - 2 + 2 = 2$$

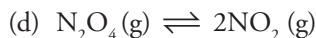


$$P = 3, C = 3, F = C - P + 2; F = 3 - 3 + 2 = 2$$

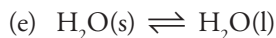


$$C = 1, P = 2; F = C - P + 2$$

$$= 1 - 2 + 2 = 1$$



$$P = 1, C = 1; F = C - P + 2 \\ = 1 - 1 + 2 = 2$$



$$P = 2, C = 1; F = C - P + 2 \\ = 1 - 2 + 2 = 1$$



$$P = 2, C = 2; F = C - P + 2 \\ = 2 - 2 + 2 = 2$$

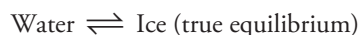
4.3 Phase Diagram

A diagram which shows the conditions of equilibrium between phases of a heterogeneous system is called a phase diagram. Phase diagrams are also called *equilibrium diagrams*. The phase diagram is a graphical representation obtained by plotting one degree of freedom against another. If the temperature (T) is plotted against pressure (P), the diagram is called a T–P diagram. If the temperature (T) is plotted against composition (C), the diagram is called a T–C diagram. Important properties of a substance like its melting point, boiling point, transition temperature and triple point can be found with the help of a phase diagram. A phase diagram is usually studied under three heads:

1. Areas or regions
2. Curves or lines
3. Points

True equilibrium It is obtained when the free energy content of a system is minimum for a given set of variables.

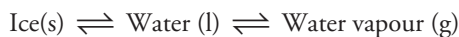
A true equilibrium exists when the same state can be approached from either direction. For example, an equilibrium between ice and water at 0 °C and at 1 atmospheric pressure is an example of a true equilibrium because this state can be achieved both by partial freezing of liquid water or by partial melting of ice.



Metastable equilibrium A state of metastable equilibrium is one that is obtained by careful approach from one direction only and can be preserved by taking care not to subject the system to shock, stirring or ‘seeding’ by the solid phase. For example, liquid water at –4 °C is said to be in a state of metastable equilibrium because this state can be achieved only by carefully cooling water below 0 °C. This state *cannot* be achieved by the fusion of ice. Moreover, if an ice crystal is added to the system, then immediate solidification occurs and the temperature rises to 0 °C.

4.4 Water System

The water system is a one-component system. It consists of three phases: ice, water and water vapour. All these are represented by one chemical entity (H_2O); hence $C = 1$.



From the phase rule, when $C = 1$,

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

That is the degree of freedom depends on the number of phases in equilibrium. Three different cases are possible:

- (i) $P = 1$; $F = 3 - 1 = 2$ (bivariant system)
- (ii) $P = 2$; $F = 3 - 2 = 1$ (univariant system)
- (iii) $P = 3$; $F = 3 - 3 = 0$ (invariant system)

The maximum number of degrees of freedom is two, hence, the phase diagram can be conveniently represented by a two-dimensional diagram on paper using pressure and temperature as variables.

The water system is shown in Figure 4.1.

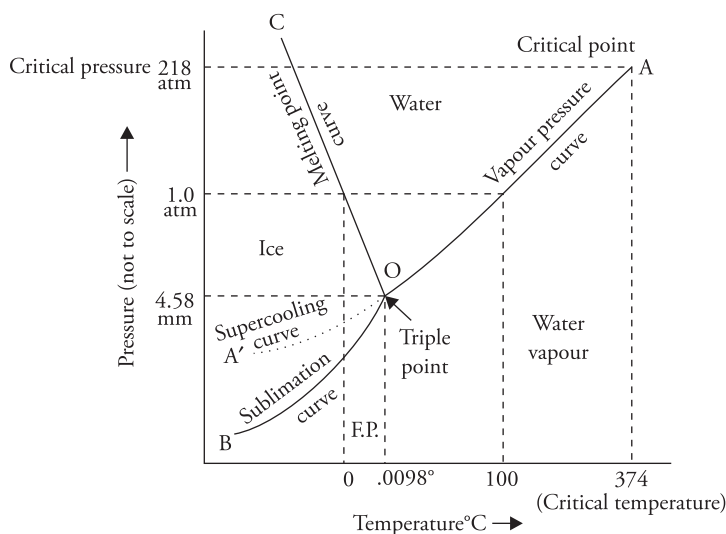


Figure 4.1 Phase diagram of water system (schematic)

It consists of the following:

- Areas** The phase diagram consists of three areas: BOC, AOC and AOB consisting of ice, liquid water and water vapour, respectively. All these three areas consist of a single phase only. Hence, according to the phase rule equation

$$F = C - P + 2 = 1 - 1 + 2 = 2 \text{ (bivariant)}$$

The system in each of these areas is bivariant which means that to locate the position of any point in these areas, it is essential to specify both the variables, that is, temperature and pressure.

2. **Curves** There are three curves in the phase diagram. Two phases exist in equilibrium along each of these curves. Hence, according to the phase rule equation

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (univariant or monovariant)}$$

The system is univariant along each of these curves which means that to locate the position of any point along these curves, only one variable, either pressure or temperature needs to be specified. The various curves in the phase diagram are as follows:

- (i) **Curve OA** This curve is known as the vapour pressure curve of water or vaporisation curve. It represents equilibrium between two phases. Along this curve, liquid water and water vapour coexist in equilibrium. The curve shows the vapour pressure of liquid water at different temperatures. The curve has its upper limit at temperature 374 °C and pressure 218 atm. This is the critical point beyond which the liquid phase merges into the vapour phase and they are no longer distinguishable from each other.
 - (ii) **Curve OB** This curve is known as the sublimation curve of ice. Two phases, ice and its vapour, coexist in equilibrium along this curve. It shows the vapour pressure of solid ice at different temperatures. The lower limit of this curve is -273 °C beyond which the vapour phase does not exist.
 - (iii) **Curve OC** This curve is known as the fusion or melting curve of ice. Two phases, ice and water, coexist in equilibrium along this curve. This curve shows how the melting point of ice varies with temperature. The curve slopes towards the pressure axis which means that the melting point of ice decreases with the increase in pressure.
3. **Triple point** The point O where all the three curves meet is known as the triple point. At the triple point, all the three phases, ice, water and water vapour, exist in equilibrium. Hence, at O, the value of $P = 3$. According to the phase rule equation

$$F = C - P + 2 = 1 - 3 + 2 = 0 \text{ (invariant or non-variant)}$$

The degree of freedom at O is zero. The equilibrium is attained at a specific temperature and pressure (0.0098 °C and 4.58 mm pressure). If either pressure or temperature is varied even slightly, then at least one of the phases will disappear and all the three phases will no longer coexist.

Metastable Curve OA' The dotted line OA' is the continuation of the vaporisation curve OA and represents the vapour pressure curve of supercooled water. This equilibrium is said to be metastable because it can be achieved only by carefully cooling water below O. This state *cannot* be achieved by the fusion of ice. Moreover, if an ice crystal is added to this system, then immediate solidification occurs and the temperature rises to 0 °C.

The water system is summarised in Table 4.1.

Table 4.1 Phase diagram of water system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C – P + 2)
Areas			
BOC (area on the left side of the curve BOC)	Solid phase (solid ice)	1	2 (bivariant)
AOC	Liquid phase (liquid water)	1	2 (bivariant)
AOB	Vapour phase (water vapour)	1	2 (bivariant)
Curves			
OA (vapour pressure curve of water or vaporisation curve)	Water \rightleftharpoons water vapour	2	1(monovariant)
OB (sublimation curve of ice)	Ice \rightleftharpoons vapour	2	1(monovariant)
OC (fusion or melting curve of ice)	Ice \rightleftharpoons water	2	1(monovariant)
OA'(super cooling curve)	Liquid \rightleftharpoons vapour	2	1(monovariant)
Points			
O(0.0098 °C, 4.58 mm)	Ice \rightleftharpoons water \rightleftharpoons vapour	3	0 (non-variant)

It is a one-component system, hence $C = 1$

4.5 Sulphur System

It is a one-component, four-phase system. The four different phases of the sulphur system are

- (i) Rhombic sulphur (S_R)
- (ii) Monoclinic sulphur (S_M)
- (iii) Liquid sulphur (S_L)
- (iv) Vapour sulphur (S_V)

As the composition of all the four phases can be represented by one chemical compound, sulphur, it is a one-component system.

When $C = 1$, then from the phase rule equation

$$F = C - P + 2; F = 1 - P + 2 = 3 - P$$

The degree of freedom for different cases will be

When

$$P = 1; F = 3 - 1 = 2 \text{ (bivariant system)}$$

$$P = 2; F = 3 - 2 = 1 \text{ (univariant system)}$$

$$P = 3; F = 3 - 3 = 0 \text{ (invariant system)}$$

$$P = 4; F = 3 - 4 = -1$$

When $P = 4$, the degree of freedom will be negative which is not possible. Therefore, all the four phases of the sulphur system can never exist in equilibrium. Only three phases can be present at a time. In the sulphur system, one solid allotropic form transforms into the other. Such a system in which two or more solid states exist in equilibrium is called a polymorphic system.

The phase diagram of sulphur system is shown in Figure 4.2.

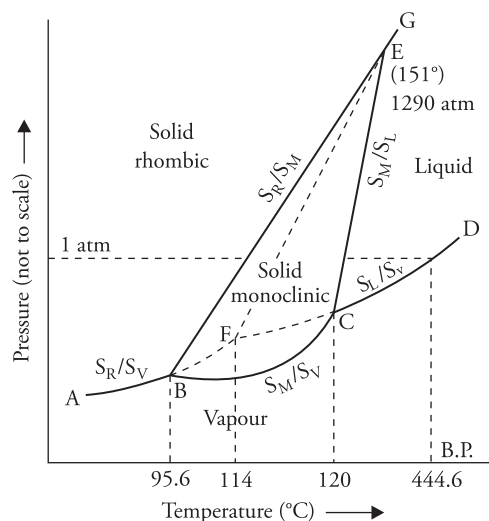


Figure 4.2 Phase diagram of sulphur system (schematic)

The phase diagram consists of the following:

1. **Areas** The phase diagram has four areas each of which consists of a single phase

- (i) ABG (rhombic sulphur)
- (ii) BECB (monoclinic sulphur)
- (iii) GECD (liquid sulphur)
- (iv) ABCD (vapour sulphur)

For each area, $C = 1$; $P = 1$, hence the degree of freedom will be

$F = 3 - 1 = 2$ (bivariant system)

Hence to locate the position of any point in these areas, both the variables—pressure and temperature—need to be specified.

2. **Curves** There are six curves in the phase diagram:

- (i) **Curve AB** It is the vapour pressure curve of rhombic sulphur. Along this curve, two phases S_R and S_V exist in equilibrium.
- (ii) **Curve BC** It is the vapour pressure curve of monoclinic sulphur. Two phases S_M and S_V exist in equilibrium along this curve.

- (iii) **Curve CD** It is the vapour pressure curve of liquid sulphur. S_L and S_V exist in equilibrium along this curve.
- (iv) **Curve BE** It is the transition curve of S_R to S_M . Along this curve, two solid phases are in equilibrium. The line BE slopes away from the pressure axis showing that the transition temperature can be raised with increase in pressure.
- (v) **Curve CE** It is the fusion curve of S_M . Monoclinic and liquid sulphur exist in equilibrium along this curve. It represents the effect of pressure on the melting point of S_M . The melting point rises with the increase in pressure. The curve ends at point E because monoclinic sulphur does not exist beyond this point.
- (vi) **Curve EG** It is the fusion curve of S_R . Rhombic and liquid sulphur exist in equilibrium along this curve.

Along all the six curves, two phases are in equilibrium. Hence the degree of freedom along these curves is

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (univariant).}$$

The system along each of these curves is univariant, hence only one variable (either pressure or temperature) is needed to express the system completely along these curves.

3. **Points** There are three stable triple points in the sulphur system: B (95.6 °C, 0.006 mm), C (120 °C, 0.04 mm) and E (151 °C, 1290 atm). Three phases exist in equilibrium along all these points.

B S_R, S_M, S_V

C S_M, S_L, S_V

E S_R, S_M, S_L

According to the phase rule equation, the degree of freedom along these triple points is

$$F = C - P + 2 = 1 - 3 + 2 = 0 \text{ (invariant or non-variant).}$$

The system corresponding to each point is non-variant. Variation of any one of the variables, temperature or pressure causes the disappearance of one of the three phases.

Metastable equilibria

Metastable curves There are three metastable curves in the phase diagram.

- (i) **Dashed curve BF** It is the vapour pressure curve of metastable S_R . If rhombic sulphur is heated rapidly, it will bypass the transition point B without changing to monoclinic sulphur and will melt at F. The metastable phases S_R and S_V are in equilibrium along this curve and the system is monovariant.
- (ii) **Dashed curve CF** It is the vapour pressure curve of supercooled liquid sulphur. If liquid sulphur is cooled rapidly, it does not change to monoclinic sulphur at point C and continues to exist as supercooled liquid. This curve represents metastable equilibrium between supercooled S_L and S_V .

- (iii) **Dashed curve FE** This is the fusion curve of metastable S_R . Along this curve, S_R and S_L are in equilibrium.

Metastable triple point F

The three metastable phases S_R , S_L and S_V are in equilibrium at this point and the system is non-variant.

The sulphur system can be summarised as given in Table 4.2.

Table 4.2 Phase diagram of sulphur system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C–P+2)
Areas			
ABG	Rhombic sulphur	1	1–1+2=2(bivariant)
BECB	Monoclinic sulphur	1	1–1+2=2(bivariant)
GECD	Liquid sulphur	1	1–1+2=2(bivariant)
ABCD	Vapour sulphur	1	1–1+2=2(bivariant)
Curves			
AB (vapour pressure of rhombic sulphur)	$S_R \rightleftharpoons S_V$	2	1–2+2=1(univariant)
BC (vapour pressure of monoclinic sulphur)	$S_M \rightleftharpoons S_V$	2	1–2+2=1(univariant)
CD (vapour pressure of liquid sulphur)	$S_L \rightleftharpoons S_V$	2	1–2+2=1(univariant)
BE (transformation curve of S_M and S_R)	$S_R \rightleftharpoons S_M$	2	1–2+2=1(univariant)
CE (fusion curve of S_M)	$S_M \rightleftharpoons S_L$	2	1–2+2=1(univariant)
EG (fusion curve of S_R)	$S_R \rightleftharpoons S_L$	2	1–2+2=1(univariant)
Metastable curves			
BF (metastable v.p curve of S_R)	$S_R \rightleftharpoons S_V$	2	1–2+2=1(univariant)
CF (metastable v.p curve of S_L)	$S_L \rightleftharpoons S_V$	2	1–2+2=1(univariant)
FE (metastable v.p curve of supercooled rhombic sulphur)	$S_R \rightleftharpoons S_L$	2	1–2+2=1(univariant)
Triple points			
B	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	3	1–3+2=0 (invariant)
C	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	3	1–3+2=0 (invariant)
E	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	3	1–3+2=0 (invariant)
F(metastable)	$S_R \rightleftharpoons S_L \rightleftharpoons S_V$	3	1–3+2=0 (invariant)

4.6 Two-Component Systems

In a two-component system ($C = 2$), the degree of freedom of a two-component system is given by

$$F = C - P + 2$$

$$F = 2 - P + 2 = 4 - P$$

When $P = 1$, the degree of freedom has the highest value.

$$F = C - P + 2$$

$$F = 2 - 1 + 2 = 3$$

It means that three variables—temperature, pressure and composition—are required to explain the system completely. Such a three-dimensional diagram cannot be expressed conveniently on paper. In order to have a single-phase diagram for a two-component system, the usual practice is to choose any two of the three variables for graphic representation, assuming the third to be constant. Hence, we can have

- (i) Pressure–temperature diagram (P – T) when composition is constant
- (ii) Temperature–composition diagram (T – C) when pressure is constant
- (iii) Pressure–composition diagram (P – C) when temperature is constant

A solid liquid equilibrium of an alloy has practically no gas phase and the effect of pressure on these equilibria is negligible. Experiments are generally conducted at room temperature. Hence in most cases, pressure is kept constant at 1 atmosphere and the phase diagram is constructed using the variables, temperature and concentration.

Thus we see that for the sake of convenience, we generally consider two variables and the third is kept constant. For example, in the solid–liquid equilibrium, usually the gas phase is absent and the effect of pressure on the system is so small that it is neglected. Such a solid–liquid equilibrium with the gas phase absent is termed as the condensed system. This will reduce the degree of freedom by one and for such a system, the phase rule becomes

$$F = C - P + 1$$

This is known as the *reduced or condensed phase rule* and is widely applicable to solid–liquid two-component systems. The solid–liquid equilibria are represented on temperature–composition diagrams.

4.7 Construction of Phase Diagrams

Thermal analysis (cooling curves)

The phase diagram of a two-component system is generally drawn by thermal analysis. Thermal analysis is the study of the cooling curves of various compositions of a system during solidification. In this method, solids of different compositions are taken at a temperature above their melting points. The resulting mixture is cooled slowly and cooling curves are constructed by plotting temperature against time.

For a mixture of definite composition, cooling curves help us to determine

1. Freezing point
2. Eutectic point

Analysis of cooling curves

- (a) **Pure substance** When a pure substance is cooled slowly and the temperature is noted at definite intervals, a curve of the type shown in Figure 4.3 is obtained. During the initial stage (part AB of the curve), the liquid cools and the fall in temperature is continuous. After this, there is a flat portion in the cooling curve from B to C. This is known as thermal arrest or temperature halt, where the temperature remains constant; the value corresponding to this is called the freezing point (T_f). The constancy of temperature continues from B, which marks the beginning of solidification, to C, which marks the end point of solidification.

Sometimes, the liquid may cool to a temperature below its freezing point before crystallisation occurs—this is called supercooling.

After the liquid has completely solidified at point C, the fall in temperature again becomes continuous (part CD of the curve) which indicates that the solid cools down further till its temperature is equal to the room temperature.

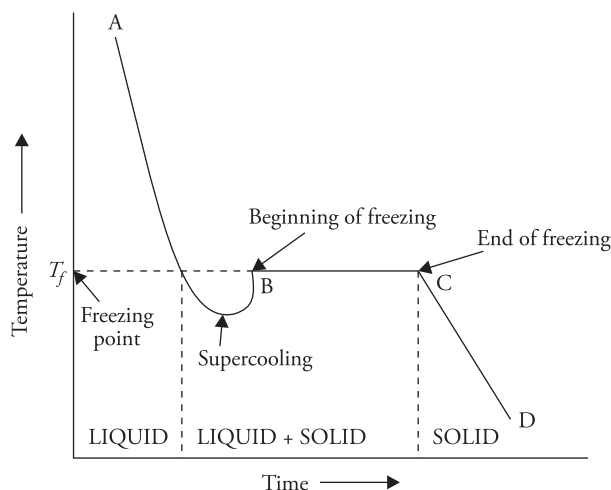


Figure 4.3 Cooling curve of a pure substance

- (b) **Mixture of two solids**

When a mixture of two solids is cooled, a continuous cooling curve is obtained initially (part AB of the curve) (Fig. 4.4). Point B marks the beginning of freezing or appearance of solid. However, the temperature does not remain constant. It decreases continuously in part BC but at a different rate. At point B, one of the components begins to solidify. During this solidification, heat is liberated and temperature falls slowly. From B to C, the composition of the mixture changes continuously. At point C, which is the eutectic point T_E (explained later), the remaining liquid solidifies as a whole, that is, both the components crystallise out separately and the temperature remains constant from C to D. After the solidification is completed, the temperature falls uniformly as represented by part DE of the cooling curve.

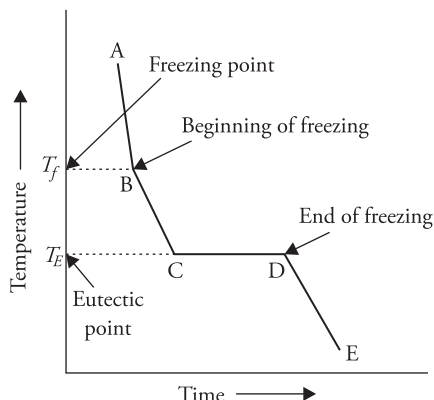


Figure 4.4 Cooling curves of mixture of two solids

Eutectic system (from the Greek word *Eutektos*, meaning easily melting, *Eu*: good, well + *tekein*: to melt): The term eutectic means ‘easy to melt’. A eutectic system is a binary system consisting of two substances which are miscible in all proportions in the liquid phase and which do not react chemically. The two substances have the tendency to lower each other’s freezing point. A solid solution of two or more substances having the *lowest freezing point* of all the possible mixtures of the components is called the *eutectic mixture*. The minimum freezing point attainable corresponding to the eutectic mixture is termed as the eutectic point (lowest melting point).

The eutectic mixture has a definite composition and a sharp melting point, that is, it melts to a liquid of the same composition. Hence, it resembles a compound. However, it is not a compound as the components are not present in stoichiometric proportions.

A binary system consisting of two substances which are miscible in all proportions in the liquid phase but which do not react chemically is known as the ‘eutectic system’, for example, a mixture of lead–silver comprises such a system.

Eutectic mixture It is a solid solution of two or more substances having the lowest freezing point of all possible mixtures of the components.

Eutectic point Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other’s freezing point and the minimum melting point attainable by the eutectic mixture is termed as the eutectic point (lowest melting point).

Examples

- A mixture of Ag and Pb of composition 97.4% Pb and 2.6% Ag with eutectic point (freezing point) at 303 °C.
- A mixture of Bi–Cd of composition 60% Bi and 40% Cd with eutectic point 144 °C

Characteristics of eutectic point

1. The system at eutectic point is invariant, the degree of freedom $F = 0$. For a two-component system, at eutectic point, $C = 2$, $P = 3$ (both the solids and their solution)

$$\begin{aligned}\therefore F &= C - P + 1 \\ &= 2 - 3 + 1 = 0\end{aligned}$$

2. It is the lowest freezing point of the system, that is, below this temperature, the liquid phase does not exist.
3. If the liquid is cooled below the eutectic point, both the components will solidify without change in composition.
4. Eutectics are mixtures and not compounds. When they were examined under an electron microscope, both the constituents are seen to lie as separate crystals. Moreover, physical properties such as density and heat of solution of eutectic solids were almost equal to the mean values of the constituents; hence, it is a mixture and not a compound.
5. The alloys of eutectic composition have greater strength than their individual components because of their crystal characteristics.

Use of eutectic system Used for creating low melting alloys which can be made into safety fuses. Safety fuse is a device containing a small piece of low melting alloy that melts under excessive heat or excessive current.

Examples

1. Safety valve in pressure cookers is made of an alloy having a definite composition and definite eutectic temperature. As the temperature rises above this temperature, the alloy melts, preventing any accident.
2. Safety fuses are employed for plugs in water sprayers in buildings. In case of accidental fires, the plugs melt away and the water is released automatically to extinguish the fire.
3. Fuse wire used in electric circuits melts away on over-heating.

Solders are readily fusible alloys which are applied to the point between metal objects to unite them closely without heating the objects to their melting point.

Examples of solders include

1. Soft solders containing 37–67% Pb, 31–60% Sn and 0.12–2% Sb, melts at low temperatures and are used for soldering electrical connections.
2. Brazing alloy containing 92% Sn, 5.5% Sb and 2.5% Cu is used for soldering steel joints.

4.8 Lead–Silver System

Lead–silver system is an example of a simple eutectic system. Silver and lead are miscible in all proportions and do not react chemically. When molten silver and lead are mixed together in all proportions, a single homogenous solution is formed. The system consists of four phases:

- (i) Solid silver
- (ii) Solid lead
- (iii) Solution of molten silver and lead
- (iv) Vapour

Since pressure has no effect on the equilibrium, the system can be represented by a temperature–concentration diagram at constant atmospheric pressure. As the gaseous phase is practically absent, one variable is neglected and the condensed phase rule

$F = C - P + 1$ will be applicable.

The phase diagram of lead–silver system is shown in Figure 4.5.

It consists of the following:

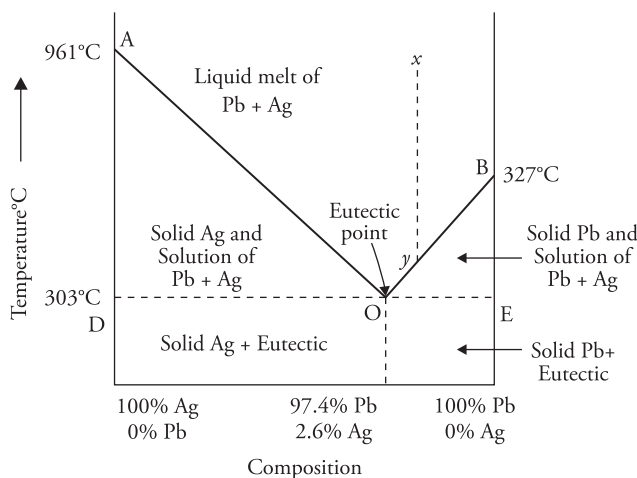


Figure 4.5 Phase diagram of lead–silver system (not to scale)

(a) Points

Point A → Freezing point of pure Ag (961 °C)

Point B → Freezing point of pure Pb (327 °C)

Point O → Eutectic point (303 °C)

(b) Curves

Curve AO → Freezing point curve of Ag on gradual addition of Pb

Curve BO → Freezing point curve of Pb on gradual addition of Ag

(c) Areas

Area above AOB

Area ADOA

Area BOEB

Area below DOE

Points In the phase diagram, point A represents the melting point of pure Ag and point B represents the melting point of pure Pb. At these points, $C = 1$, $P = 2$ (pure Ag in equilibrium with its liquid or pure Pb in equilibrium with its liquid); hence, $F = C - P + 1$; $1 - 2 + 1 = 0$.

Curves It is clear from the diagram that addition of Pb to pure Ag lowers the melting point of Ag; similarly, addition of Ag to pure Pb lowers the melting point of Pb.

The curve AO represents the melting point of Ag on gradual addition of Pb. Along this curve, solid Ag and solution are in equilibrium.

The curve BO represents the melting point of Pb on gradual addition of Ag. The curve indicates that the melting point of Pb gradually falls on addition of Ag. Along this curve, solid Pb and solution are in equilibrium.

Both AO and BO represent univariant systems

$$C = 2 \quad P = 2$$

$$F = C - P + 1 \quad ; \quad 2 - 2 + 1 = 1$$

Areas

Area above AOB It consists of only one phase (liquid solution). On applying the reduced phase rule equation, the degree of freedom comes out to be two. Hence, the system is bivariant and both temperature and composition are required to be specified to define the system completely

$$\begin{aligned} C = 2, \quad P = 1 \quad F &= C - P + 1 \\ &= 2 - 1 + 1 = 2 \end{aligned}$$

Area ADOA It contains two phases—solid Ag and solution containing Pb and Ag

Area BOEB It represents the phases—solid Pb + solution containing Pb and Ag. Both these areas have two phases and are univariant.

$$\begin{aligned} F &= C - P + 1 \quad C = 2 \text{ (Pb and Ag)} \\ &= 2 - 2 + 1 = 1 \quad P = 2 \text{ (Liquid + solid phase)} \end{aligned}$$

Area below DOE It represents a solid mixture of Pb or Ag with eutectic. The number of phases is 2 (either Ag or Pb + eutectic) and the system is univariant.

$$\begin{aligned} C = 2, P = 2 \quad F &= C - P + 1 \\ &= 2 - 2 + 1 = 1 \end{aligned}$$

Eutectic point O

The two curves AO and BO intersect at point O at a temperature of 303 °C. The point O is known as the eutectic point. At this point, three phases—solid Ag, solid Pb and the melt are in equilibrium. On applying the phase rule equation, we get

$$\begin{aligned} F &= C - P + 1 \\ &= 2 - 3 + 1 = 0 \end{aligned}$$

Thus, the system at this point is invariant. Both temperature (303 °C) and composition (Ag 2.6% and Pb 97.4%) are fixed at this point. If the temperature is increased above the eutectic point, the solid phase (silver or lead) will disappear and if the temperature decreases below the eutectic point, the solution phase disappears and only the solid phase (eutectic + solid lead or silver) will remain.

The various areas, curves, and points on the Pb–Ag phase diagram are tabulated in Table 4.3.

Table 4.3 Phase diagram of lead –silver system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) (C–P+1)
AO (freezing point curve of Ag on addition of Pb)	Crystallisation of Ag begins $\text{Ag (s)} \rightleftharpoons \text{liquid}$	2	$2 - 2 + 1 = 1$ (univariant)
BO (freezing point curve of Pb on addition of Ag)	Crystallisation of Pb begins $\text{Pb (s)} \rightleftharpoons \text{liquid}$	2	$2 - 2 + 1 = 1$ (univariant)
Area above AOB	Liquid phase (solution of Pb + Ag)	1	$2 - 1 + 1 = 2$ (bivariant)
Area below DOE	Solid mixture (eutectic + solid Ag or Pb)	2	$2 - 2 + 1 = 1$ (univariant)
Area ADOA	Solid Ag in equilibrium with liquid having composition given by the curve OA	2	$2 - 2 + 1 = 1$ (univariant)
Area BOEB	Solid Pb in equilibrium with liquid having composition given by the curve OB	2	$2 - 2 + 1 = 1$ (univariant)
Point O (eutectic point)	Solid Ag, solid Pb and their solution coexist	3	$2 - 3 + 1 = 0$ (invariant)

Application of Ag–Pb system

Pattinson's process for desilverisation of argentiferous lead The process of heating argentiferous lead containing a very small quantity of Ag (0.1% by mass) and cooling it to get pure lead and liquid rich in silver is called Pattinson's process.

Argentiferous lead is first heated to a temperature above its melting point. The system consists of only the liquid phase represented by point *x* in Figure 4.5. It is then allowed to cool. The temperature of the melt will fall along the perpendicular line *xy* without change in composition. As the point *y* is reached, lead will begin to crystallise and the percentage of silver will increase in the solution. The system moves along the curve *yo*. The melt continues to be richer and richer in silver until the point O is reached. At point O, the percentage of silver is 2.6% by mass.

After removing the lead that separates out, the liquid is cooled further to give a mixture of eutectic composition (97.4% Pb + 2.6% Ag). Pure silver is obtained from this alloy by other processes like cupellation.

Difference between melting point, triple point and eutectic point

- At melting point, a solid is in equilibrium with a liquid of the same composition.
- At triple point, three phases are in equilibrium.
- At eutectic point, two solids and a liquid are in equilibrium.

By definition, all eutectic points are melting points but the reverse is not true. Similarly, all eutectic points are triple point and not vice versa.

Two-component system which forms a stable compound with congruent melting point

If the two-components of a system at a certain stage enter into chemical combination with one another forming stable compounds, the compound formed may have congruent melting point.

A compound is said to have congruent melting point when it melts sharply at a constant temperature into a liquid of the same composition as that of the solid from which it is derived, for example, zinc–magnesium system.

4.9 Zinc–Magnesium System

It is an example of a two-component system in which two metals form a compound having congruent melting point. The compound is an alloy having the formula $\text{Mg}(\text{Zn})_2$ with a melting point of 590°C , which lies between the melting point of the two metals.

The melting point of zinc is 420°C and that of magnesium is 651°C . $\text{Mg}(\text{Zn})_2$ is stable and melts without change in composition.

As the experiment is carried out at constant pressure and the vapour phase is not considered, the condensed phase rule will be applied.

$$F = C - P + 1$$

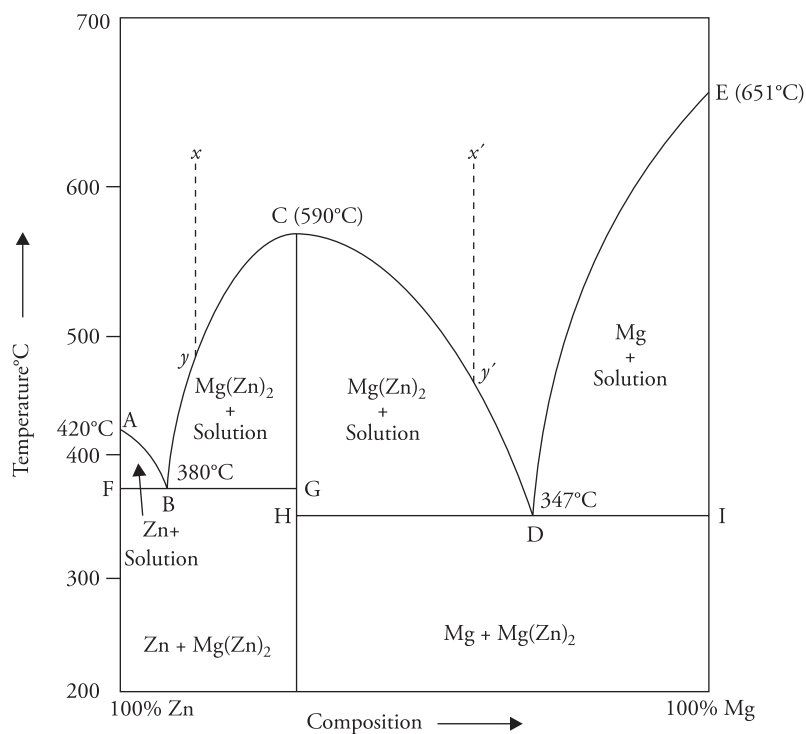


Figure 4.6 Phase diagram of zinc–magnesium system (not to scale)

Molar composition at B is 79% Zn and 21% $\text{Mg}(\text{Zn})_2$

Molar composition at D is 61% $\text{Mg}(\text{Zn})_2$ and 39% Mg

The phase diagram (Fig. 4.6) consists of the following:

(a) Points

Point A → Freezing point of zinc (420 °C)

Point E → Freezing point of magnesium (651 °C)

Point C → Freezing point of Mg (Zn)_2 (590 °C)

Point B → Eutectic point (380 °C)

Point D → Eutectic point (347 °C)

(b) Curves

Curve AB → Freezing point curve of zinc on gradual addition of magnesium

Curve ED → Freezing point curve of magnesium on gradual addition of zinc

Curve BC and CD → Freezing point curves of Mg (Zn)_2

(c) Areas

Area ABFA

Area CBGC

Area CHDC

Area EDIE

Area below FBG

Area below HDI

Area above ABCDE

Points

In the phase diagram, point A represents the melting point of pure zinc. Point E represents the melting point of pure magnesium and point C represents the melting point of Mg (Zn)_2 . At each of these points, the value of $C = 1$, $P = 2$ (solid in equilibrium with the liquid of the same composition)

$$\text{Hence, } F = C - P + 1; 1 - 2 + 1 = 0$$

All these three points are invariant with zero degree of freedom.

Curves

Curve AB It is the freezing point curve of Zn. On gradual addition of Mg to Zn, the melting point of zinc is lowered along the curve AB. Along this curve, solid zinc is in equilibrium with the solution containing Zn and Mg. Thus, the number of phases is two. Applying the condensed phase rule,

$$F = C - P + 1; 2 - 2 + 1 = 1$$

Thus the system is univariant.

Curve ED It is regarded as the freezing or melting point curve of magnesium on gradual addition of zinc. Addition of zinc lowers the melting point of magnesium along the curve ED. Along this curve, magnesium is in equilibrium with a solution of Zn and Mg and the system is univariant.

Curve CB It represents the lowering of melting point of Mg (Zn)_2 on addition of zinc.

Curve CD It represents the lowering of melting point of Mg (Zn)_2 on addition of magnesium. The curves CB and CD are univariant.

Areas

Area ABFA The area contains solid zinc and liquid containing zinc and magnesium

Area CBGC In this area, Mg (Zn)_2 and molten Zn and Mg are present

Area CHDC This area also contains Mg (Zn)_2 and molten zinc and magnesium

Area EDIE This has two phases—solid magnesium and liquid containing zinc and magnesium.

In all the above areas, a solid is in equilibrium with the solution. Hence, $P = 2$.

$$F = C - P + 1 \quad ; \quad 2 - 2 + 1 = 1$$

The system in these areas will be univariant.

Area below FBG It represents a solid mixture of zinc and Mg (Zn)_2 , Hence $P = 2$.

$$F = C - P + 1 \quad ; \quad 2 - 2 + 1 = 1$$

Area below HDI It represents a solid mixture of magnesium and Mg (Zn)_2 . Again $P = 2$.

$$F = C - P + 1 \quad ; \quad 2 - 2 + 1 = 1$$

Area above ABCDE It represents a single phase consisting of molten zinc and magnesium.

$$P = 1; \quad C = 2 \quad F = C - P + 1 \quad ; \quad 2 - 1 + 1 = 2 \quad \text{The system is bivariant}$$

Eutectic points There are two eutectic points B and D. At B, the three phases are zinc, Mg (Zn)_2 and their melt. The eutectic temperature at B is 380°C and the composition is 79% Zn and 21% Mg (Zn)_2 , whereas at D, the three phases are magnesium, Mg (Zn)_2 and melt. The temperature at D is 347°C and the composition is 61% Mg (Zn)_2 and 39% Mg.

$$\text{Therefore, } C = 2; \quad P = 3 \quad ; \quad F = C - P + 1$$

$$2 - 3 + 1 = 0 \quad \text{The system is invariant.}$$

Cooling Consider a melt of composition represented by a point x . Allow it to cool along the line xy . When it reaches y , the solid Mg (Zn)_2 separates out from the melt and the composition varies along the curve yB . At this point, there are two phases, and hence the system becomes univariant.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

Similarly, if a melt of composition x' is cooled, the temperature will fall to y' without change in composition. At point y' , Mg (Zn)_2 separates and the composition varies along the curve $y'D$. At D, magnesium also separates out.

The phase diagram of the Zn–Mg system can be considered to be made up of two simple eutectic diagrams side by side, one on the left of CG and the other on its right. The curves BC and CD should meet to give a sharp point at C. The rounded maxima indicate that the compound formed is not very stable and dissociates partly. The dissociation of products in the liquid phase depresses the actual melting point of the compound resulting in a rounded melting point.

The various areas, curves, and points on the Zn–Mg phase diagram are tabulated in Table 4.4.

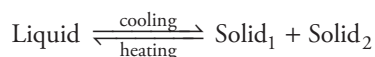
Table 4.4 Phase diagram of zinc-magnesium system

Region of the phase diagram	Phases in equilibrium	Number of phases (P)	Degree of freedom (F) $F = C - P + 1$
Point A, freezing point of Zn	$\text{Zn (s)} \rightleftharpoons \text{Zn(l)}$	2	$1 - 2 + 1 = 0$
Point E, freezing point of Mg	$\text{Mg (s)} \rightleftharpoons \text{Mg(l)}$	2	$1 - 2 + 1 = 0$
Point C, freezing point of Mg(Zn)_2	$\text{Mg(Zn)}_2 \text{ (s)} \rightleftharpoons \text{Mg(Zn)}_2 \text{ (l)}$	2	$1 - 2 + 1 = 0$
Point B, eutectic point	Zn, Mg(Zn)_2 and solution	3	$2 - 3 + 1 = 0$
Point D, eutectic point	Mg, Mg(Zn)_2 and solution	3	$2 - 3 + 1 = 0$
Areas:			
ABFA	Solid Zn + liquid containing Zn and Mg	2	$2 - 2 + 1 = 1$ (univariant)
CBGC	Solid Mg(Zn)_2 + molten Zn and Mg	2	$2 - 2 + 1 = 1$
CHDC	Solid Mg(Zn)_2 + molten Zn and Mg	2	$2 - 2 + 1 = 1$
EDIC	Solid Mg + liquid containing zinc and magnesium	2	$2 - 2 + 1 = 1$
Area below FBG	Solid mixture of Zn + Mg(Zn)_2	2	$2 - 2 + 1 = 1$
Area below HDI	Solid mixture of Mg + Mg(Zn)_2	2	$2 - 2 + 1 = 1$
Area above ABCDE	Molten zinc and magnesium	1	$2 - 1 + 1 = 2$ (bivariant)

4.10 Iron–Carbon Alloy System

Before delving into the details of the iron–carbon alloy system, the student needs to familiarise with the different types of binary phase diagrams.

- Binary isomorphous phase diagrams** – The two metallic components of such phase diagrams are completely miscible in each other in both liquid and solid states. They are represented by temperature as ordinate and chemical composition as abscissa. The upper line of the diagram is called the *liquidus* above which only liquid phase exists and the lower line is the *solidus* below which only solid phase is found (Fig. 4.7). The region between the solidus and the liquidus has both solid and liquid phase and the composition can be determined by drawing a horizontal line called the *tie line* at the temperature of interest.
- Binary eutectic phase diagrams** – They are phase diagram of two-components which are completely miscible as liquids and may be either totally insoluble as solids (Bi–Cd system) or partially miscible in each other as solids (Pb–Ag system). A eutectic is defined as a phase transformation in which the liquid phase transforms simultaneously into two solid phases.



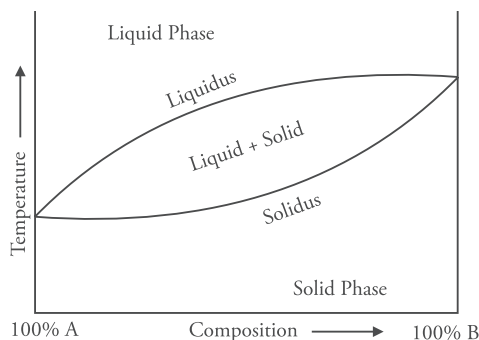
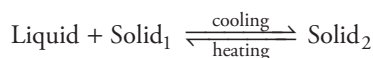
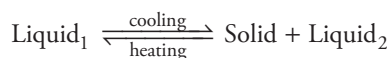


Figure 4.7 Binary isomorphous phase diagram

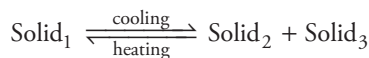
3. **Binary peritectic phase diagram** – In a peritectic system, two phases which are already present in a heterogeneous mixture react together to produce a third phase and in this process one or both the original phases disappear.



4. **Monotectic system** – In these transformations the liquid phase on cooling forms a solid phase and a new liquid phase of different composition.



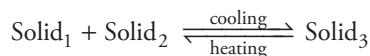
5. **Eutectoid system** – It is the transformation where a solid phase is converted into two or more intimately mixed solids on cooling.



The composition at the temperature at which the transformation occurs is called the eutectoid composition.

The iron–carbon alloy system is a practical example of the eutectoid system where the FCC iron austenite (a solid solution of carbon in γ iron) decomposes to form pearlite – an intimate mixture of ferrite α -iron and carbide (cementite).

6. **Peritectoid system:** It is a system in which a solid phase reacts with another solid phase to yield a third solid phase on cooling.



The iron carbon phase diagram consists of the different systems mentioned above. The iron carbon phase diagram is a two-component system consisting of Fe and Fe_3C (iron carbide),

hence it is a phase diagram of Fe – Fe₃C as most steels contain only Fe₃C rather than carbon (graphite).

When molten iron is cooled, it freezes at 1538 °C into δ -ferrite form. In the solid state, iron exhibits polymorphism—existing in different crystal forms at different temperatures.

- Between 1538 °C and 1400 °C it acquires a BCC structure and this is termed as δ -iron.
- It changes into FCC structure between 1400 °C and 910 °C.
- Below 910 °C it again acquires a BCC structure and this form of iron is termed as α -iron.

The different phases of pure iron are shown in Figure 4.8.

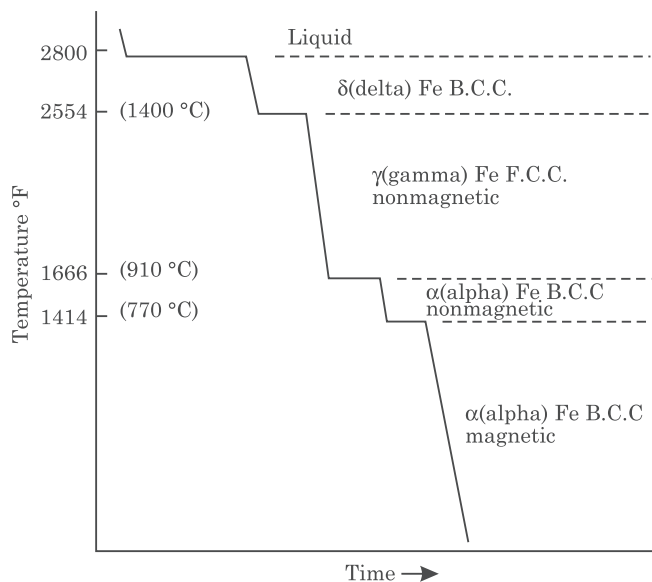


Figure 4.8 Cooling curve of pure iron

The iron–carbon phase diagram consists of the following phases and microstructures:

- Ferrite** It is α -iron with BCC structure. It is pure, soft iron containing only 0.008% carbon at room temperature. It is soft, ductile and remains strongly magnetic till 768 °C (Curie point). On further heating, it becomes non – magnetic. α -iron is stable upto 910 °C and it contains maximum 0.025% carbon at 723 °C.
- Austenite** It is a solid solution of carbon in gamma iron (γ -iron) with FCC structure. It is soft, ductile but stronger and less ductile than ferrite. It is non-magnetic. It exists at temperature above 723 °C and dissolves up to 2% carbon and is stable between 723 °C and 1493 °C. On cooling below 723 °C it transforms into pearlite – an intimate mixture of ferrite α -iron and carbide (cementite).
- Cementite** It is interstitial carbide of iron (Fe₃C) containing about 6.67% carbon. It is extremely hard, brittle and is magnetic below 200 °C. It is an important constituent as the brittleness and hardness of cast iron depends upon the amount of cementite present in it.

- (iv) **Pearlite** It is an intricate mixture of ferrite and cementite. It is lustrous and has a pearl like appearance. It has a lamellar structure and consists of alternate layers of ferrite and cementite (87% ferrite and 13% cementite). Pearlite is formed by cooling austenite below 723 °C. Actually steel with 0.8% carbon is wholly pearlite which represents eutectoid steel. Steel with less than 0.8% carbon is called hypoeutectoid steel and steel with carbon content greater than 0.8% is called hypereutectoid steel. The former contains ferrite and pearlite and is soft whereas the latter contains pearlite and cementite and is hard and brittle.
- (v) **Ledeburite** This consists of two phases—austenite and cementite. When liquid alloy containing 4.3% carbon is cooled below 1148 °C ledeburite is obtained. It represents the eutectic transformation at 1148 °C.

The phase diagram of this system is shown in Figure 4.9.

Point A It represents the melting point of pure iron (1538 °C). A peritectic transformation occurs at 1493 °C (point J) with δ iron giving γ iron containing 0.18% carbon.

Curve AC It is the freezing point curve of iron. On gradual addition of carbon, the melting temperature of iron decreases as the percentage of carbon increases up to point C, which is the eutectic point. The point C corresponds to the temperature 1148 °C. At point C, which is the eutectic point, eutectic transformation occurs with the formation of ledeburite containing 4.3% carbon (ledeburite represents the eutectic composition at the eutectic point).

Curve ACB Above the line ACB, the iron–carbon alloy will be wholly liquid. Thus, the curve ACB is called the liquidus. In the area above ACB, iron and carbon are present in liquid solution. Thus, there is only one phase in this area.

Curve AECD Below AECD, the alloy will be wholly solid. Thus, the line AECD is called solidus.

Loop AECA Inside the loop AECA, the alloy austenite is partly liquid and partly solid.

Loop BCD Inside the loop BCD, there are two phases, cementite (solid) and liquid.

Area DCESKD This area contains a mixture of austenite and cementite (both are solids).

Area AESGA In this area, the alloy is a solution of austenite in iron.

Area GSL In the small triangular area GSL, we get a mixture of ferrite and austenite.

Eutectic point C The eutectic point at C corresponds to the lowest melting point, below which the liquid solidifies completely. At C austenite (γ) and cementite (Fe_3C) precipitate out simultaneously. The mixture at eutectic point with Fe_3C containing 4.3% carbon is termed as ledeburite.

Eutectoid point S: S is another point and this corresponds to 723 °C. Above 723 °C, there is a solid solution of austenite in iron. When cooling starts from point Q along QS, the solid solution of austenite in iron will cool down without decomposing up to the point S. At S eutectoid transformation occurs and two solids ferrite and cementite precipitate out simultaneously. The mixture of ferrite and cementite at eutectoid point S containing 0.8% carbon is termed as pearlite which is the eutectoid steel. To the left of eutectoid steel is hypoeutectoid steel (a mixture of pearlite and ferrite) and to the right is the hypereutectoid steel (a mixture of pearlite and cementite).

The important points of iron–carbon phase diagram are summarised in Table 4.5.

The eutectoid (pearlite with 0.8% carbon) and eutectic (ledeburite with 4.3% carbon) are considered as independent structural constituents, which can influence the properties of alloys.

Moreover steels are alloys containing upto 2% carbon whereas cast iron contains 2.3% to 6.7% carbon. However alloys of iron with carbon content greater than 4.6% have poor applications in fabrication, casting and production of ferrous alloys.

Figure 4.8 gives the phase diagram of iron–carbon alloy system.

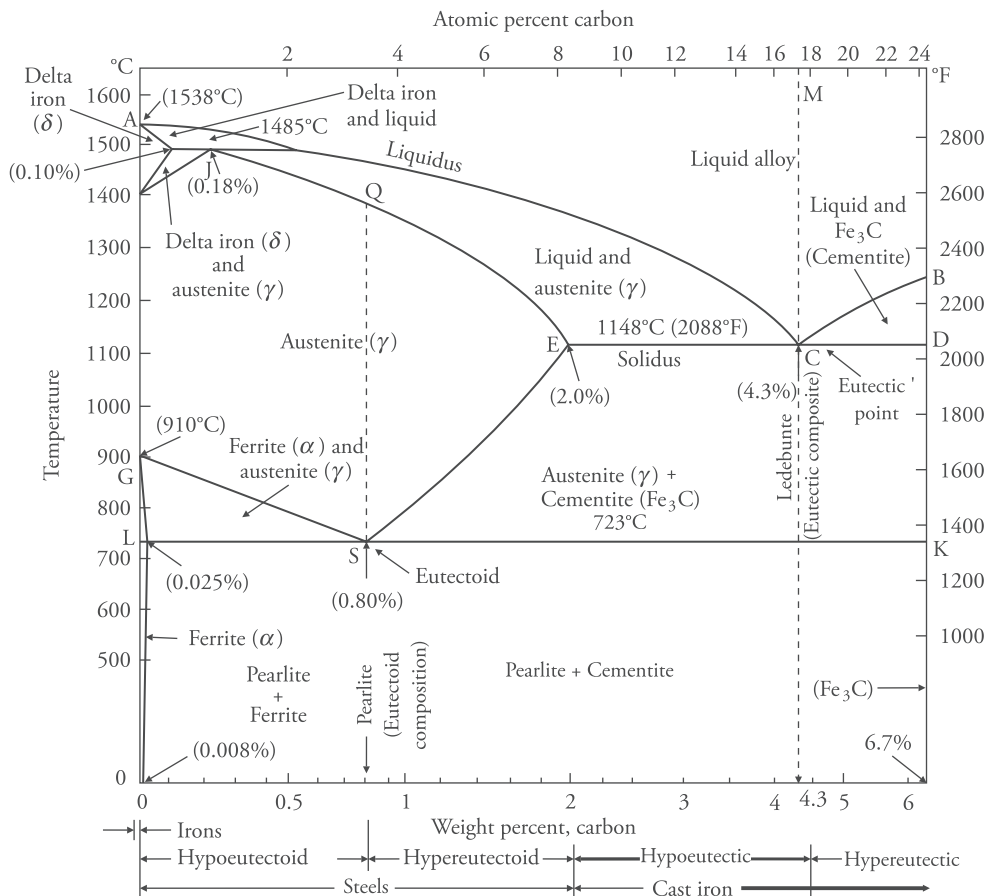


Figure 4.9 Phase diagram of iron–carbon system

Table 4.5 Important points in the iron–carbon phase diagram

Point	Reaction involved
J (1493 °C) (Peritectic point)	$\delta \text{ iron} + \text{Liquid} \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{Austenite (solid solution of carbon in } \gamma \text{ iron)}$
C (1148 °C) (Eutectic point)	$\text{Liquid} \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{Austenite} + \text{Cementite}$ (ledeburite with 4.3% carbon is the eutectic mixture)
S (723 °C) (Eutectoid point)	$\text{Austenite} \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{Ferrite} + \text{Cementite}$ (pearlite with 0.8% carbon is the eutectoid mixture)

Solved examples

1. What metal will separate out when a liquid alloy of copper and aluminium containing 25% copper is cooled, if the eutectic mixture includes 32.5% Cu? How many grams of that metal can be separated from 200 g of the alloy?

Solution

The alloy contains 25% Cu and hence it will have 75% Al.

∴ 200 g of alloy will contain 50 g Cu and 150 g Al.

In an eutectic mixture,

Let the eutectic mass formed = x g

It is given that the eutectic contains 32.5% Cu and hence 67.5% Al.

Since the percentage of Cu in the alloy is less than that in the eutectic, all the copper present in the alloy will be included in the eutectic.

Therefore, Al separates out when the alloy is cooled.

Further, if 100 g of eutectic is formed, then Cu in it is 32.5 g. In other words, if 32.5 g of Cu is present in the alloy, 100 g of eutectic is formed. Therefore, if 50 g of Cu is present, the eutectic formed

$$= \frac{50 \times 100}{32.5} = 153.85 \text{ g}$$

∴ The eutectic formed, $x = 153.85$ g

$$\begin{aligned} \text{The weight of Al separated out} &= \text{Total wt of the alloy} - \text{wt of the eutectic formed} \\ &= (200 - 153.85) \text{ g} \\ &= 46.15 \text{ g} \end{aligned}$$

2. An alloy of tin and lead contains 78% tin. Find the mass of eutectic in 1 kg of solid alloy, if the eutectic contains 64% tin.

Solution

1 kg alloy contains 780 g tin and 220 g lead. In the eutectic composition, tin is 64%, hence lead will be 36%.

Therefore, corresponding to 220 g of lead, the mass of tin in eutectic

$$= \frac{220 \times 64}{36} = 391.11 \text{ g}$$

∴ Total mass of eutectic in alloy = $220 + 391.11 = 611.11$ g

3. An alloy of Cd and Bi contains 25% Cd. Find the mass of eutectic in 1kg of alloy, if the eutectic contains 40% Cd.

Solution

Eutectic composition = 40% Cd and 60% Bi

Given 1 kg of alloy contains 250 g Cd and 750 g Bi

∴ Corresponding to 250 g of Cd, the mass of Bi

$$= \frac{250 \times 60}{40} = 375 \text{ g}$$

Hence total mass of eutectic in 1kg alloy = 250 + 375 = 625 g

4. 1000 kg of a sample of argentiferous lead containing 0.1% silver is melted and then allowed to cool. If the eutectic contains 2.6% Ag, what mass of (i) eutectic will be formed and (ii) mass of lead will separate out?

Solution

Mass of Ag in 1000 kg argentiferous lead

$$= \frac{0.1 \times 1000}{100} = 1 \text{ kg}$$

$$\therefore \text{Mass of eutectic} = \frac{1 \text{ kg} \times 100\%}{2.6\%} = 38.46 \text{ kg}$$

$$\begin{aligned} \text{(ii) Mass of Pb separated} &= (1000 - 38.46) \text{ kg} \\ &= 961.54 \text{ kg} \end{aligned}$$

5. An alloy AB of 10 g weight contained A at 25%. The molten AB on cooling gives out B and a eutectic alloy with A and B at equal percentage. What amount of B is formed?

Solution

∴ The alloy contains 25% A

$$\therefore \text{Weight of A in 10 g alloy} = \frac{25 \times 10}{100} = 2.5 \text{ g}$$

$$\text{Weight of B in 10 g alloy} = 10 - 2.5 = 7.5 \text{ g}$$

On cooling, eutectic containing equal amount of A and B separate. Hence, the eutectic contains 2.5 g of A and 2.5 g of B

∴ Amount of B formed

$$= \text{Original amount} - \text{Amount of B in eutectic}$$

$$= 7.5 \text{ g} - 2.5 \text{ g} = 5.0 \text{ g}$$

4.11 Metal and Alloys

Introduction

Metals occupy a very important place in our life. They have played a key role in the progress of human civilisation, from the pre-industrial age to the present age. They constitute the major part of the periodic table and they along with their alloys make up the backbone of all engineering products. Metals are divided into two categories—ferrous and non-ferrous. Fe, Mn, Cr and their alloys fall in the category of ferrous metal while the rest are all non-ferrous metals.

Metals are found in nature in combined form as oxides, sulphates, sulphites, carbonates, etc. They can be extracted by applying the principles of metallurgy.

4.12 Properties of Metals

The utility of metals in industry depends on their distinct physical properties which makes them useful for specific industries. These properties influence qualitatively and quantitatively the response of a given material to factors like temperature, magnetic field, electric current, radiations, pressure, etc. The selection of a metal for a particular use depends on its properties. The important properties of metals are given below.

- a. Physical properties
- b. Thermal properties
- c. Mechanical properties
- d. Magnetic properties
- e. Electrical properties
- f. Chemical properties
- g. Technological properties.

a. Physical properties

Physical properties of a material include its dimensions, appearance, colour, density, melting point, porosity, etc.

- (i) *Appearance* Metals differ in their appearance. Aluminium is silvery white, copper is brownish. Some metals are lustrous, some are dull. Wrought iron has a red scaly appearance, whereas mild steel has a smooth finish with a bluish black sheen.
- (ii) *Colour* Different metals have different colours which depend on the wavelength of light absorbed by them. Iron is grey, tin is silvery white, gold is yellow and so on.
- (iii) *Density* It is the weight of a unit volume of the metal. A metal can be light or heavy depending upon its density.
- (iv) *Melting point* The temperature at which a metal changes into molten state is its melting point. The use of metals in industry depends on their melting points.

- (v) *Porosity* It is the ratio of the volume occupied by pores to the volume of a material. A metal is said to be porous if it has pores in it. Porous metals trap air, hence their density is low but they are resistant to changes in temperature.

b. Thermal properties

Thermal properties study the response of a material to the application of heat. The important thermal properties of a metal are as follows:

- (i) *Heat capacity* Heat capacity is indicative of a material's ability to absorb heat from the surroundings. It represents the amount of heat energy required to raise the temperature by unity.
- (ii) *Specific heat* It is the quantity of heat added to a unit mass to raise its temperature by one degree.
- (iii) *Thermal expansion* It is the change in dimension of a metal in response to thermal energy and is measured in terms of coefficient of thermal expansion. The coefficient of thermal expansion is the expansion in unit length of a substance when the temperature rises by one degree.
- (iv) *Melting point* It has been discussed earlier under physical properties.
- (v) *Thermal conductivity* It is the rate at which heat can flow through a material under the influence of a given temperature gradient.
- (vi) *Thermal shock resistance* It is defined as the ability of a metal to withstand sudden and severe changes in temperature without failure.
- (vii) *Thermal stability* Under normal conditions, a metal is subjected to temperature fluctuations. Thermal stability refers to the ability of a metal to withstand those changes without undergoing any permanent change in dimensions, without cracking or peeling off.

c. Mechanical properties

These properties describe the behaviour of a metal under the action of external forces. The various mechanical properties are as follows.

- (i) *Elasticity* A material tends to get deformed under load. Elasticity is defined as the ability of a material to seek its original dimensions when the deforming force is removed.
- (ii) *Plasticity* It is the property of a material by virtue of which it may be permanently deformed when subjected to an external force great enough to exceed the elastic limit. Plasticity is the reverse of elasticity.
- (iii) *Toughness* It is the ability of a material to withstand bending or torsion without fracture.
- (iv) *Resilience* It is the ability of a material to return to its original form when the stretching, bending or compressing force is removed.
- (v) *Tensile strength* It refers to the force needed to fracture a material. It is the ratio of the maximum load to the original cross-sectional area. Its unit is kg/cm². It is an important basis for fixing the working stresses especially in case of brittle materials.

- (vi) *Shear strength* It is the property which enables a material to withstand forces acting upon it with a tendency to distort its shape.
- (vii) *Ductility* It is the property of a metal by virtue of which it can be drawn into wires. Silver is the most ductile of all metals.
- (viii) *Malleability* It is the property by virtue of which a metal can be beaten into sheets by hammering or rolling. Gold is the most malleable metal.
- (ix) *Brittleness* It is the opposite of toughness and is the property of a material which does not permit permanent deformation without breakage. A brittle material breaks into pieces as soon as it is dropped from a height (glass is brittle material).
- (x) *Hardness* It is the resistance of a material to plastic deformation by indentation. Hardness is the stiffness which enables the metal to resist scratching, abrasion or cutting. Diamond is the hardest known mineral.
- (xi) *Fatigue* When a material is subjected to repeated loads or stresses, it develops a characteristic behaviour which is different from its behaviour under steady load. Fatigue is the phenomenon that leads to fracture under such conditions and fatigue resistance is the property which enables a material to overcome fatigue. Annealing increases the fatigue resistance of a material.
- (xii) *Creep* It is the continuous deformation of a machine part by the action of load at elevated temperatures. Machines like steam generators are exposed to static mechanical stress at elevated temperatures. Deformation under such conditions is called creep. A substance with high creep resistance can be used comfortably at high temperature.
- (xiii) *Wear resistance* Wear is the unintentional removal of solid material from the surface by rubbing action. Wear resistance is defined as the ability to resist wear and abrasion.

d. Magnetic properties

Magnetic properties refer to the behaviour of the substance under a magnetic field. It is important for materials like transformer iron, etc. Metals may exhibit diamagnetic, paramagnetic, ferromagnetic behaviour. A substance is said to be magnetic if it is attracted by magnets. Examples include Fe, Co, Cr and Mn. Diamagnetic substances like Cu, Zn, Pb and Sb are weakly repelled by a magnet. These properties are important for determining their industrial end uses.

e. Electrical properties

The selection of metal and material for electric equipments is done on the basis of their electrical properties. Metals are generally good conductors of electricity. Copper and silver are used for making electric wires because of their good conductivity.

f. Chemical properties

Metals tend to suffer chemical deterioration on coming in contact with other substances. The important chemical properties of metals are their corrosion resistance, chemical composition, reactivity, acidity and alkalinity, etc.

g. Technological properties

Technological properties are those properties which influences the processing of metal and their alloys during industrial operations. The important technological properties are:

- (i) *Castability* Castability is that complex property of a metal or alloy which allows it when molten, to fill a mould and give a flawless casting.
- (ii) *Machinability* A metal is considered machinable if it can be machined by a given tool with little energy at high speed without unduly reducing the life of the tool and resulting in a finished smooth surface.
- (iii) *Weldability* It is the capacity of a material to be welded under the given fabrication conditions of heat and pressure and perform satisfactorily in the intended service.
- (iv) *Workability/ formability* The workability of a metal is a very broad subject and deals with its capacity to be rolled, drawn, casted, hardened, heated and recrystallised without any permanent deformation or change in its properties.

4.13 Alloys

An alloy is a homogeneous mixture of two or more elements with metallic properties or a metal and a non-metal possessing metallic properties. Chemically, alloys are solid solutions and are harder, more malleable and have lower melting points than the component elements. The properties of a metal can be modified by alloying it with some other element. Important elements that form alloys are copper, zinc, lead, tin, nickel, aluminium, chromium and tungsten.

4.14 Purpose of Making Alloys

A pure metal may not have all the properties required for the desired end use. These properties like strength, malleability, ductility and electrical conduction can be improved by alloying it with other metals or non-metals. The main purposes of alloying are given below.

- a. **To increase the hardness of the metal:** Pure metal may not be very hard, their hardness can be improved by alloying them with some other metal or non-metal. For example, pure gold is very soft and cannot be used for making ornaments. Alloying it with copper improves its hardness and makes it suitable for the preparation of ornaments. Similarly, pure iron is very soft. Its hardness can be improved by alloying it with 0.15–1.5% carbon in the form of steel. The iron–carbon alloy known as steel has a hardness greater than the individual components.
- b. **To lower the melting point:** As it is well known, adding impurity to a pure metal reduces its melting point. Hence, the melting point of an alloy is much lower than its constituent elements. Alloying makes the metal easily fusible. Wood metal, an alloy of lead, bismuth, tin and cadmium melts at 60.5 °C which is far below the melting point of any of the individual elements.
- c. **To improve corrosion resistance:** Pure metals are quite reactive and have a tendency to get corroded by reacting with environmental gases, moisture and other components. Pure

iron gets rusted easily but stainless steel, an alloy of iron with carbon and chromium resists corrosion.

- d. **To improve castability:** A metal is good for casting if it expands on solidification and produces a hard and fusible product. Metals like lead expand on solidification but are soft and brittle. When alloyed with 5% tin and 2% antimony to yield an alloy called *type metal*, it becomes fusible, expands on solidification and has exceptionally good casting properties. This alloy finds use for casting printing type.
- e. **To modify chemical activity:** Chemical activity of a metal can be modified by alloying it with a suitable element. For example, the chemical activity of sodium reduces on alloying with mercury to form sodium amalgam, whereas the activity of aluminium increases on alloying it with mercury.
- f. **To modify colour:** The colour of a metal can be modified by alloying it with a suitable metal or non-metal. For example, aluminium bronze, an alloy of copper and aluminium, has a beautiful golden yellow colour and brass, an alloy of copper (red) and zinc (silver-white), is yellow in colour. The colour of gold may be modified by alloying with different metals, for example: Red gold: 75% gold, 25% copper; rose gold: 75% gold, 22.25% copper, 2.75% silver; pink gold: 75% gold, 20% copper, 5% silver; white gold formulation consists of 90% gold and 10% nickel. Copper can be added to increase malleability; green gold is a mixture of 75% gold and 25% silver.

4.15 Classification of Alloys

Alloys can be classified in a number of ways.

1. **Based on the base metal in the alloy:** On the basis of the principal metal in the alloy, alloys are termed as aluminium alloy, ferrous alloy, magnesium alloy, copper alloy, lead alloy, tin alloy, etc.
2. **Based on the application of alloy:** Alloys are classified on the basis of their application. For example, alloys used for soldering are solder alloys, others are bearing alloys, etc.
3. **Based on metallurgical structure:** Alloys are classified on the basis of their structure and the number of phases. For example, brass (30% Zn, 70% Cu), monel metal (66.6% Ni, 33.3% Sn) and transformer iron (96% Fe, 4% Si) are single phase alloys and muntz metal (60% Cu, 40% Zn) is a two phase alloy.
4. **Based on method of fabrication:** Alloys are also classified on the basis of the type of fabrication, easy machinability and pressure tightness. For example, copper alloy contains 5–40% Zn, while casting alloy contains 5% Sn, 5% Zn and 5% Pb.

Ferrous alloys These alloys contain iron as one of the major components. Common ferrous alloys are steel and cast iron. Steel and cast iron are alloys of iron with carbon and other admixtures like Mn, P, S, Cr, Si, etc. These alloys differ in carbon content. The carbon content in steel is not more than 1.3% while cast iron may contain 1.7–4.0% carbon.

Cast iron It is an alloy of iron with carbon and silicon. Its approximate composition is C = 2.5–3.8%, Mn = 0.15%, Si = 0.4 – 1.0%, P and S = 0.1%, remaining iron

Properties

The carbon present in cast iron exists partly as free carbon and partly in combined form as cementite Fe_3C . When molten iron from the blast furnace is suddenly cooled, the carbon remains in the form of cementite and we get a white crystalline form of iron known as white cast iron. On the other hand, if molten iron is allowed to cool slowly, the carbon separates as graphite and a softer variety called grey cast iron is obtained.

Cast iron is hard, brittle and therefore cannot be welded. It is good for casting because it expands on solidification and can be cast into any desired shape in a sand mould.

Applications

It does not rust easily and hence is used for making parts generally exposed to weather such as gutter pipes, lamp posts, manhole covers, sanitary wares, gas or water pipes, for underground purposes, machine tool structures, rolling mill and general machinery parts, frames of electric motors, household appliances, etc.

Wrought iron

It is obtained from cast iron by heating it on the hearth of a reverberatory furnace. It is a mechanical mixture of very pure iron and a silicate slag. Its approximate composition is C = 0.02–0.03%, P = 0.05–0.25%, Si = 0.02–0.10%, S = 0.008–0.02%, Mn = nil–0.02%, slag = 0.05–1.5%, iron = balance amount

Properties

Wrought iron has high ductility, high resistance towards corrosion, high resistance towards fatigue. It can overcome sudden and excessive shock without permanent injury. It is malleable, ductile and can be rolled into bars.

Uses

Wrought iron is available in the form of plates, sheets, bars, pipes, tubings, casings, etc. It is widely used for the following.

1. Underground service lines and electrical conduits in building construction.
2. Railing of bridges, drainage lines, sewer outfall lines, sludge tanks and lines.
3. In rail, road and marine works like tanker heating coils, diesel exhaust and air brake piping.
4. In other activities like gas collection hoods, cooling tower, spray pond piping etc.

Steel: Plain carbon steel is an alloy of iron and carbon with the percentage of carbon ranging between 0.5–1.5%. It is malleable and its hardness depends upon the amount of carbon present in it. Steel containing low percentage of carbon (0.05–0.30%) is called *mild steel*. It possesses the properties of wrought iron with the elasticity and hardness of steel. It is used for making steel wires, sheets, rivets, screws, pipes, nails, chains, etc.

Medium carbon steel: The percentage of carbon varies from 0.3–0.70%. It is used for making parts that are subjected to shock and heavy reversal stress like railway coach axles, crank pins on heavy machine, crankshafts, die blocks, valve springs, cushion rings, and etc.

High-carbon steel: The percentage of carbon is 0.7–1.5%. It is hard and is also called *hard steel*. It is used for making rock drills, railway rails, punches and dies, machine chisels, keys, pins, railway springs, mandrels, files, metal cutting tools, paper knives, metal cutting saws, wire drawing dies, etc.

Alloy steel

Steel is considered to be alloy steel when it contains small quantities of elements such as Al, B, Cr, Co, Mo, Ni, Ti, W, V or any other element, added to it to obtain the desired properties.

Purpose of alloying

The main purposes of alloying steel are to improve:

1. Corrosion resistance
2. Hardness
3. Strength
4. Ability to undergo milling operations like rolling, drawing, pressing, hammering, etc.
5. Ductility
6. Toughness
7. Wear resistance
8. Cutting ability
9. Tensile strength
10. Ability to retain physical properties at high temperature
11. Resistance to abrasion
12. Elasticity

4.16 Special Effects of Alloying Elements

Carbon The carbon content in steel affects its hardness, tensile strength, melting point and ability to undergo machining operation.

Nickel It increases toughness, resistance to impact, strengthens steels, lessens distortion in quenching, and improves elasticity, ductility as well as corrosion resistance.

Chromium It improves toughness and hardness simultaneously. Chromium combines with carbon to form chromium carbide which improves resistance to abrasion and wear.

Silicon It improves oxidation resistance and strengthens low alloy steel.

Titanium It prevents localised depletion of chromium in stainless steel during long heating.

Molybdenum It imparts hardness, improves resistance to abrasion, raises tensile strength and creep strength at high temperature, counteracts tendency towards temper brittleness.

Vanadium It imparts strength and toughness to heat treated steel, enhances tensile strength, ductility and shock resistance.

Tungsten Increases hardness, toughness, abrasion resistance, shock resistance and imparts high strength in tempering.

Manganese Increases strength, toughness, counteracts brittleness from sulphur; if it is present in high percentage with carbon content in steel, then it lowers both ductility and weldability.

Copper 0.2 to 0.5% copper when added to steel increases resistance to atmospheric corrosion and acts as a strengthening agent.

Cobalt Improves mechanical properties such as tensile strength, fatigue strength, hardness, heat resistance and also imparts freedom from cracking and distortion.

4.17 Alloy Steels and Their Applications

The different types of alloy steels are as follows:

- a. **Heat resisting steels** These steels contain molybdenum, manganese and chromium. Chromium improves the corrosion resistance of such steels at high temperature and molybdenum provides strength as well as creep resistance to steel at high temperature.

Nichrome A steel containing 10% Ni and 20% Cr can be used up to 1100 °C. Steels with 0.06–0.15% carbon and 15–20% chromium are resistant to oxidation up to 900 °C.

Uses These steels find use in making equipments that are exposed to high temperature like boiler parts, retorts, steam pipes, gas turbines, annealing chambers, outlines of furnaces, etc.

- b. **Corrosion resistant steels** They are known as stainless steels and are resistant to corrosion by chemicals and atmosphere. These steels contain chromium, molybdenum and nickel as the alloying agents. Formation of a dense chromium oxide film on the surface of the metal prevents corrosion of the metal. Stainless steel containing more than 16% chromium resists corrosion very effectively. Stainless steel is of two types.

- *Heat treatable stainless steels* They contain a maximum of 1.2% carbon and about 12–16% chromium. They are tough, magnetic, water and weather resistant and can be used up to a temperature of 800 °C. They find use in making blades, cutlery, scissors and surgical instruments.
- *Non-heat treatable stainless steel* They are more resistant to corrosion, but exhibit poor strength at high temperatures. Depending upon their composition, they can be magnetic as well as non-magnetic.

- c. **Non-magnetic stainless steel** They contain less than 0.15% carbon, 8–21% nickel and 18–26% chromium. Steels containing 18% Ni have maximum corrosion resistance. Addition of molybdenum further improves resistance to corrosion. These steels find use in making sinks, utensils, dental and surgical instruments, decorative pieces, etc.

- d. **Magnetic stainless steel** Steels with iron, nickel, cobalt and rare earth elements exhibit strong magnetism and are used for making pole pieces of electromagnets, dynamos, motors, loud speakers, transformer cores, etc.

Alnico An aluminium–nickel–cobalt steel is used for making powerful electromagnets. Its composition is 20% Ni, 12% Al, and 6% Co.

- e. Tool steels** Tool steels should have considerable hardness, wear resistance, toughness and mechanical strength. They are used for making tools like dies, hammers, shears, etc. Cutting tools are made of steels containing 4–21% tungsten, 1–2% vanadium and 4–4.5% chromium in addition to 0.5–0.75% carbon. These steels are also termed as *high speed steels* (HSS). Different types of high speed/tool steels are as follows;
- (i) *Tungsten steel* The most commonly used high speed steel used for making cutting tools is made of high tungsten alloy. A popular variety of high speed steel contains 18% tungsten, 4% chromium, 1% vanadium and 0.7% carbon. Tungsten forms carbides and prevents the softening of the alloy at high temperature; hence, this steel has the ability to maintain a sharp cutting edge even at red heat. Such steels are therefore used for making lathes, shapers, cutters, drills, bits, planers and for making permanent magnets, etc.
 - (ii) *Molybdenum HSS* These steels also contain chromium and nickel. The approximate composition of these steels is 0.15–0.30% molybdenum, 0.5–0.80% chromium and 1.5–2.0% nickel. These steels retain hardness at red heat and possess great toughness. Molybdenum HSS are used in cutting tools such as gears, bearings, axles, shafts, aircraft landing gears and automobiles parts. Fatigue resistance of molybdenum–nickel steels is generally high.
 - (iii) *Vanadium HSS* These steels containing over 1% vanadium and 0.7% carbon have excellent abrasion resistance. Chrome vanadium steel contains 0.8–1.1% chromium, 0.25–0.35% carbon and less than 0.25% vanadium. They find use in axles, shafts, aeroplanes, automobiles and locomotives where great resistance to fatigue, great strength and toughness is required.
 - (iv) *Cobalt HSS* Cobalt tool steel (5–8% cobalt) is used where high frictional heats are developed. Cobalt imparts additional red hardness to steel and the cutting ability to the steel is maintained at elevated temperatures.
- f. Nickel steels** Of all the alloy steels, nickel steel is the most extensively used. Nickel improves toughness, ductility, tensile strength, impact resistance, elasticity, heat and corrosion resistance of steel and confers greater shearing strength to steel. Nickel steels are divided into many groups (Table 4.6).

Table 4.6 Different groups of nickel steel

Group	Composition	Properties	Uses
Nickel steel	2.5–3.5% nickel and 0.1–0.15% carbon	—	Pipes, sheets, rivets and stocks for case hardening
Nickel steel	3.5% nickel and 0.2–0.4% carbon	Good tensile strength, good elasticity and hardness, have corrosion resistance and low coefficient of expansion	For making axles, gears, heavy guns, bolts, aeroplane parts, air screws.
Nickel steel	25–28% nickel, 1–4% manganese, 0.5% chromium and 0.3–0.5% carbon	Can tolerate temperature up to 800 °C	Used in steam turbine blades, valves for internal combustion engines, electrical resistance wires, etc

Invar steels	30–36% nickel, 0.3–0.5% carbon	Almost zero coefficient of thermal expansion	Meter scale, measuring tapes, clock pendulums, survey instruments, wheels of balances and scientific measuring devices.
Platinite	46% nickel and 0.15% carbon	Coefficient of expansion is almost similar to glass	Used in armoured glass, i.e., glass plates containing steel nets, wires in electric bulbs, etc.
Parmolloy	80% nickel and no carbon	High magnetic permeability	Used in communication engineering
Nickel chromium steels	1–3.5% nickel, 0.5–1.5 chromium and 0.2–0.55% carbon.	They combine the effect of nickel in increasing toughness and ductility and chromium in improving hardening ability and wear resistance	Depending upon the relative ratio of Ni, Cr and C, these steels are used for making armour plates of battle ships, projectiles, gun barrels, automobile parts, aeroplane parts, gears, balls and rollers for bearings and for making steels for lockers intended to keep money and valuables safe

- g. **Chromium steels** They contain 2–11% chromium. Steels with less than 2% Cr are generally hard and wear resisting while those with more than 11% chromium are stainless steels. Chromium intensifies the effect of rapid cooling on steels and therefore, is used only in steels which are to be heat treated. It improves hardness, wear resistance, increases tensile strength and corrosion resistance. Steel containing 8% Cr is used for electrical purposes and that with 15% Cr finds use in springs, ball and rolling bearings. The compressive strength of chromium steels is exceptionally high. They can be of different types.
- Chromium vanadium steels** Their approximate composition is 0.8–1.1% chromium, 0.25% vanadium and 0.35–0.9% carbon. They are shock-resistant steels and absorb sudden shock; hence, they are also called *spring steels*. They possess high elasticity and have great impact resistance. Such steels are used for leaf springs, coil springs and laminated springs.
 - Chromium molybdenum steels** These steels contain C = 0.35%, Cr = 1.06%, Mo = 0.36%. They are easy to roll and draw into tubes, to fabricate, to weld; therefore, they are very popular for airplane structural parts.
- h. **Manganese steels** They contain Mn = 1.6–1.9%, C = 0.18–0.48%, Si = 0.2–0.35%, S and P ≤ 0.04% each. Manganese increases hardness, tensile strength, resistant to abrasion, shock absorbing capacity. Steel with 1–8% Mn are useful for making non-deforming tool steels. Mn steel finds use in making parts subjected to shock and excessive wear like crushing machines, crossing of railway rails, bullet proof helmets, armour plates, steam shovels, buckets, etc.
- i. **Silicon steels** They contain 0.7–4.0% silicon and possess greater hardness, improved corrosion resistance, increased electrical resistance, magnetic permeability and good casting qualities. They find use in making springs, transformer cores, and pole pieces of electromagnets.

- j. **Duriron** They contain 12–14% silicon and are very hard and extremely resistant to corrosion by acids and alkalis. They have excellent casting properties. They are used for making pipes, valves, fittings, retorts and so on used in acid and alkali industries.
- k. **Marageing steels** These steels have very high yield and tensile strength, high-notch toughness and good ductility. They are melted and cast under vacuum from high purity material. Their approximate composition is Ni = 18%, Ti = 0.2–0.6%, Al = 0.1–0.2%, Co = 8–9%, Mo = 3–5%, C = 0.003%.

4.18 Non-Ferrous Alloys

These alloys do not contain iron as one of their main components. Copper, aluminium, lead, magnesium, nickel, tin, zinc and cobalt are the main components of non-ferrous alloys. They find widespread applications due to the following properties:

- Easy to work, ductile, malleable, good formability.
- High thermal and electrical conductivity.
- Resistance to fatigue, abrasion and corrosion.
- Good machinability, easy castability.
- Low density.

The composition, properties and uses of some non-ferrous alloys is given below.

Copper alloys Copper finds extensive use in the manufacture of electric transmission cables and electric appliances due to their high electrical conductivity. Next to steel, copper and its alloys are the most important engineering materials. The alloys of copper can be classified under two major categories.

- Brasses (copper and zinc alloys)
- Bronzes (copper–tin alloys) and aluminium bronzes (copper–aluminium alloys)

Apart from these two types, copper can also be alloyed with small quantities of various alloying elements.

Various important copper alloys are presented in Table 4.7.

Table 4.7 Different types of copper alloys

Alloy	Composition	Properties	Uses
Gilding metal	5–15% Zn, balance copper	Red to brassy yellow or golden colour, stronger and harder than pure copper	For making coins, medals, tokens, fuse caps, jewellery and many decorative items
Cartridge brass	70% Cu and 30% Zn	Greater percentage elongation and tensile strength, soft, ductile, harder and stronger than copper	Used for cartridges and shell cases, for caps of electric lamps, bulbs, door furniture, household articles, etc.

Dutch metal	Cu 80%, Zn 20%	Golden yellow in colour and is suitable for drawing and forming operations	Battery caps, flexible hoses, tubes, name plates and cheap jewellery
Admiralty brass	Cu 71%, Zn 28%, Sn 1%	Small amount of tin improves corrosion resistance	Propellers and marine works
German silver	Cu 25–50%, Zn 10–35%, Sn 5–35%	Malleable, ductile, resistant to corrosion by sea water, possesses good strength and shines like silver	Corrosion resistant screws and equipments, utensils, jewellery, coins and decorative items.
Muntz metal or yellow metal	Cu 60%, Zn 40%	A very good hot working material	Use as brazing alloy for steel, other applications are in ship sheathing, valve stems, architectural work, condenser tubes etc.
Naval brass	Cu 60%, Zn 39.25%, Sn 0.75%	Corrosive resistant, especially in contact with sea water	Used for structural applications and forging especially in cases where contact with sea water is likely to induce corrosion, also used in propeller shafts, valve stems, pump impellers, etc.
Bronzes	Alloy of copper and elements other than nickel or zinc	Corrosion resistant, hard, resists surface wear and possesses superior mechanical properties. Can be shaped into wire, rod and sheets	
Different type of bronzes are given below.			
Phosphor bronze	Sn = 10–13%, P = 0.4 to 10%, rest copper	High strength and toughness, resistant to corrosion, low coefficient of friction	Bearings, making pump parts, lining, springs, diaphragms, gears, clutch discs, bellows, etc.
Aluminium bronze	Cu 90–93%, Al = 10–7%	Strong, fusible, resistant to corrosion even at high temperatures, possesses good abrasion resistance, has a magnificent yellow colour	Used in bearings, gears, slide valves, imitation jewellery, valve seats, propellants, pulp parts, etc.
Silicon bronze	Si = 1–4% Fe = 0.5–1.0% Mn = 0.25–1.25% Cu = balance	High strength and toughness as that of mild steel and corrosion resistance as that of copper. It can be cast, rolled, forged and pressed hot and cold	For bearings, marine hardware, boiler parts, die cast parts, roll mill sleepers, turntable bushings

Gun metal	Cu = 85%, Zn = 4%, Sn = 8%, Pb = 3%	Hard, tough, strong enough to resist the force of explosion	Bearings, steam pipe fittings, marine castings, hydraulic valves and gears, foundry works
Coinage bronze	Cu 89–92%, Sn 8–11%	Soft, ductile and durable	Utensils, coins, statues, wires, pumps, valves

Aluminium and its alloys

Aluminium is a light weight silvery white metal with density about one-third that of steel or brass. Pure aluminium is not very strong; it forms high strength alloys in conjunction with metals like Cu, Cr, Ni, Fe, Zn, Mn, Si and Mg. Aluminium alloys are used extensively in

- Transportation industry, engine parts, hardware, doors and window frames, fittings.
- Components on train, trucks, buses, automobiles, cars and aeroplanes use aluminium alloys.
- In the food industry, aluminium foils are used for packing; they are used in making equipment like pans, pressure cookers, storage containers, shipping containers, etc.

The important alloys of aluminium are:

- Duralumin* Al = 95%, Cu = 4%, Mn = 0.5% and Mg = 0.5%. Duralumin has high machinability, high tensile strength after heat treatment, strength as high as steel but has only one-third of its weight; it has excellent casting and forging properties.

Uses It is extensively used in aircraft industry as alclad (duralumin clad on either side of pure aluminium); due to high ductility and good electrical conductivity, it finds use in making surgical instruments, cables, fluorescent tube caps, etc.

Other important non-ferrous alloys are presented in Table 4.8.

Table 4.8 Non-ferrous alloys

Alloy	Composition	Properties	Uses
Magnalumin	Al 70–90%, Mg 30%	Strong, tough, lighter than aluminium with mechanical properties similar to brass	Aeroplane parts, cheap balances and scientific instruments
Solders	Low melting point alloys of Cu and Sn	They melt at low temperature	Soldering electric connections, sealing tin cans, soldering steel joints by fusing
Type metal	Pb 75%, Sb 20%, Sn 5%	Expands slightly on solidification and is very good for casting	Production of printer's type
Rose metal	Bi 50%, Pb 28%, Sn 22%	Fuses readily; has low melting point 89 °C	Used for making fire alarms, fuse wires, casting for dental works and in automatic sprinkler systems
Constantan	Ni 45%, Cu 55%	Highest electrical resistivity, lowest temperature coefficient of resistance	Used for electrical resistors, thermocouples, wheatstone bridges, etc.

Monel	Ni 66%, Cu 31.5%, Fe 0.9%, Mn and other elements: traces	Strong, bright in appearance, excellent resistance to atmospheric and sea water corrosion, resistant to acids, less resistant to alkalis	Architectural and marine applications where corrosion resistance is important, also used in food, pharmaceutical, paper, oil and chemical industries
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4.19 Heat Treatment of Steel

Heat treatment is a process involving a sequence of heating and cooling operations in steel (or any other metal alloy) to obtain a desired combination of properties.

Heat treatment produces the following effects in the properties of metals:

- Relieves the metal of internal stresses.
- Improves machinability.
- Refines grain size and makes the metal structure homogeneous.
- Improves ductility, toughness, resistance of material to heat, wear, shock and corrosion.
- Improves electrical, thermal and magnetic properties of the metal.

Heat treatment alters the physical properties of the metal alloys without affecting its chemical properties.

Some common heat treatment processes employed for steel are

- Annealing
- Normalising
- Hardening
- Tempering

Heat treatment process

First, the steel is heated to a high temperature so that it is converted to the austenite phase. It is then kept at this temperature for some time to permit homogenisation of the material. After the formation of homogeneous austenite throughout, the alloy is cooled. The rate of cooling depends upon the properties required in steel. If there is need, steel can be reheated and cooled again. The heat treatment processes are discussed below.

Annealing

Annealing is the process of heating steel to a high temperature (up to austenite phase) and then cooling it carefully under controlled conditions. Annealing makes the following physical changes in steel.

- The internal stresses caused due to uneven contraction during casting are relieved.
- It reduces hardness
- It improves machinability
- Refines the grain structure
- Helps in the removal of trapped gases.

There are two types of annealing.

- a. Process annealing or low temperature annealing
 - b. Full annealing or high temperature annealing
- a. **Process annealing (stress relieving)** It is low-temperature annealing in which steel is heated to a temperature below its critical point and then cooled slowly. Process annealing helps to remove the internal stress in steel. It is generally applied to hypoeutectoid steel and is carried out at a temperature below the eutectic temperature (550–650 °C). As there is no phase change during process annealing, ferrite and cementite (Fe_3C) are present in the microstructure throughout the process.
 - b. **Full annealing** In full annealing, steel is heated to a temperature of about 30–50 °C above the upper critical temperature (to austenite phase) and held at this temperature for a sufficiently long time. It is then gradually cooled to room temperature simply by switching off the furnace. The annealing temperatures of mild steel, medium carbon steel and high carbon steel are 840–870 °C, 780–840 °C and 760–780 °C, respectively. After full annealing, the microstructure of hypoeutectoid steels consists of proeutectoid ferrite and pearlite.

Full annealing helps to refine grains, remove strains from forgings and castings, induces softness, improves machinability, formability and also improves electrical and magnetic properties of steel.

Normalising It is also known as air quenching. In this process, steel is heated to 40–50 °C above its upper critical temperature, held at this temperature for a short time and then cooled in still air at room temperature. Air cooling is faster than the furnace cooling, hence the cooling time in normalising is much lower than in annealing.

Like annealing, normalising also results in the formation of ferrite, cementite and lamellar pearlite, but the micro structure of pearlite produced is finer than in the fully annealed state resulting in the formation of slightly harder and stronger materials.

The purpose of normalising is

- To produce a uniform structure
- Refine grain size of steel
- Reduce internal stress
- Produce harder and stronger steel than full annealing
- Improve the engineering properties of steel

Hardening of steel Hardening is the rapid cooling of steel by immersing it in a liquid bath such as water or air. The process is also known as quenching. It increases the hardness, strength and wear resistance of steel. In this process, steel is heated to 30–50 °C above the upper critical temperature, held at this temperature for sometime (soaking period) and then cooled rapidly or quenched in a suitable medium like water, oil, brine or molten salt bath. Due to rapid cooling, carbon remains in solution and austenite transforms to martensite. Hardened steel is in a stressed condition and hence it is very brittle. It cannot be used for practical purposes; hence hardening is followed by tempering.

Tempering: In tempering, the quenched steel is reheated to a predetermined temperature (200 °C for high-carbon steel and 400–650 °C for steel containing 0.35–3.5% carbon), then it is allowed to cool slowly. This reduces the hardness and brittleness of steel and increases its toughness and ductility. For better ductility and toughness, the tempering temperature should not exceed 400 °C.

Tempering reduces the stress and strains that develop due to quenching. It is always applied to cutting tools like blades, chisels, cutters and tool bits.

Summary

- The phase rule was given by Gibbs and explains the equilibrium existing in heterogeneous systems. It states that the equilibrium between different phases is influenced by temperature, pressure and concentration only and not by gravity, electrical or magnetic forces. The number of degrees of freedom (F) is related to the number of components (C) and phases (P) by the phase rule equation

$$F = C - P + 2$$

- **Phase** A phase is a homogenous, physically distinct and mechanically separable portion of a system which is separated from other parts of the system by a definite boundary.
- **Component** The number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation.
- **Degrees of freedom** The number of degrees of freedom of a system is the minimum number of independent variables of a system, such as temperature, pressure and concentration which can define a system in equilibrium completely.
- Phase diagrams are also called equilibrium diagrams. A true equilibrium exists when the same state can be approached from either direction. Metastable equilibrium is obtained by the careful approach from one direction only.
- Water system is a one-component system with three phases in equilibrium.
- Sulphur system is a one-component system with four phases, however only three phases can exist in equilibrium. It exhibits polymorphism—two solid states (rhombic sulphur and monoclinic sulphur) interconvert into one another.
- A two-component system is represented on a pressure–composition diagram. Since the reactions occur at atmospheric pressure, pressure is assumed to be constant and the phase rule reduces to $F = C - P + 1$
- A eutectic system is a binary system consisting of two substances which are miscible in all proportions in the liquid phase and which do not react chemically.
- A solid solution of two or more substances having the *lowest freezing point* of all the possible mixtures of the components is called the *eutectic mixture*. The minimum freezing point attainable corresponding to the eutectic mixture is termed as the eutectic point (lowest melting point).
- Lead–silver system is an example of a eutectic system having four phases—solid silver, solid lead, solution of silver and lead, and their vapour.
- Zinc–magnesium system is a two-component system with a congruent melting point.

- Iron–carbon alloy system is a two-component system with the following phases—ferrite, cementite, austenite, pearlite and ledeburite.
- An alloy is a homogeneous mixture of two or more elements with metallic properties or a metal and a non-metal possessing metallic properties.
- Alloys help to improve the mechanical, thermal, physical, magnetic, electrical, chemical and technological properties of a metal.
- Alloys may be ferrous alloys and non-ferrous alloys. Ferrous alloys have iron as the major component and non-ferrous alloys can be copper alloys, aluminium alloys, nickel alloys, etc.
- Plain carbon steel is an alloy of iron and carbon with the percentage of carbon in the range 0.5–1.5%. Steel is considered to be alloy steel when it contains small quantities of elements such as Al, B, Cr, Co, Mo, Ni, Ti, W, V or any other element added to it to obtain the desired properties.
- Heat treatment is a process involving a sequence of heating and cooling operations in steel (or any other metal alloy) to obtain a desired combination of properties.
- Some common heat treatment processes employed for steel are annealing, normalising, hardening, tempering.
- Annealing is the process of heating steel to a high temperature (up to austenite phase) and then cooling it carefully under controlled conditions.
- Normalising is also known as air quenching. In this process, steel is heated to 40–50 °C above its upper critical temperature, held at this temperature for a short time and then cooled in still air at room temperature.
- Hardening is the rapid cooling of steel by immersing it in a liquid bath such as water or air.
- In tempering, the quenched steel is reheated to a predetermined temperature (200 °C for high carbon steel and 400–650 °C for steel containing 0.35–3.5% carbon), then it is allowed to cool slowly.

Review Questions

1. State the Gibbs phase rule. With the help of suitable examples, explain the terms
(i) Component (ii) Degree of freedom (iii) Phase.
2. What is a phase diagram? Explain the phase diagram of the water system and discuss the importance of triple point.
3. With the help of a well labelled diagram, explain the sulphur system in detail. Explain why in a sulphur system, all the four phases cannot exist in equilibrium.
4. Write short notes on
(i) Condensed phase rule (ii) Triple point
(iii) Eutectic system (iv) Eutectic point
(v) True and metastable equilibrium

5. Explain the lead–silver system. How can this system be applied to the process of desilverisation of argentiferous lead?
6. What is a congruent melting point? Explain the zinc–magnesium system with the help of a suitable phase diagram.
7. Explain the cooling curves of a pure substance and a mixture of two solids.
8. Write a detailed description of the various physical properties of metal. How does alloying help to alter the properties of metals?
9. What is an alloy? How are alloys classified?
10. What are ferrous alloys? Explain the properties and applications of cast iron, wrought iron and steels.
11. What are alloy steels? What are the special effects of various alloying elements in steels?
12. Explain in detail the various alloy steels and their applications.
13. What are non-ferrous alloys? Explain the properties and applications of the common non-ferrous alloys.
14. Explain the iron–carbon alloy phase diagram.
15. What do you understand by heat treatment of steels? Explain the various processes used in the heat treatment of steel and their significance.

Multiple Choice Questions

1. Phase rule seeks to explain equilibrium existing in
 - (a) Homogeneous equilibria
 - (b) Heterogeneous equilibria
 - (c) Both homogeneous and heterogenous equilibria
 - (d) Neither homogeneous nor heterogeneous equilibria
2. Gibbs phase rule states that

(a) $F = C + P + 2$	(b) $F = C - P - 2$
(c) $F = C - P + 2$	(d) $F = P - C + 2$
3. The number of phases in equilibrium at triple point are

(a) One	(b) Two
(c) Three	(d) Four
4. When an equimolar mixture of ammonium chloride is heated, it changes into vapour



The number of phases and components in the system are

- | | |
|--------------------------|--------------------------|
| (a) 2 and 1 respectively | (b) 2 and 2 respectively |
| (c) 1 and 2 respectively | (d) 1 and 1 respectively |

5. In the above example, if NH_3 and HCl are not present in equivalent amounts, then the number of phases and components will be
 - (a) 2 and 1 respectively
 - (b) 2 and 2 respectively
 - (c) 1 and 2 respectively
 - (d) 1 and 1 respectively
6. Homogeneous physically distinct and mechanically separable parts of a heterogeneous system are called
 - (a) Components
 - (b) Phases
 - (c) Degrees of freedom
 - (d) States of the system
7. The number of stable triple points in a sulphur system are
 - (a) One
 - (b) Two
 - (c) Three
 - (d) Four
8. Unsaturated solution of NaCl in water is a
 - (a) One-phase one-component system
 - (b) One-phase two-component system
 - (c) Two-phase one-component system
 - (d) Two-phase two-component system
9. The lowest freezing point attainable for a two-component system is called its
 - (a) Freezing point
 - (b) Eutectic point
 - (c) Solidification point
 - (d) None of the above
10. For a Pb-Ag system, the eutectic point and composition of the mixture at eutectic point are
 - (a) 303°C and 97.4% Pb and 2.6% Ag
 - (b) 144°C and 60% Pb and 40% Ag
 - (c) 285°C and 85% Pb and 15% Ag
 - (d) 150°C and 75% Pb and 25% Ag
11. The number of phases in a Pb-Ag system is
 - (a) One
 - (b) Two
 - (c) Three
 - (d) Four
12. The existence of a solid in more than one crystalline form is called
 - (a) Heterogeneity
 - (b) Polymorphism
 - (c) Allotropy
 - (d) Isotropy
13. Alloying helps to improve
 - (a) Mechanical properties
 - (b) Thermal properties
 - (c) Technological properties
 - (d) All the above
14. Which of the following is not a single phase alloy?
 - (a) Brass
 - (b) Muntz metal
 - (c) Monel metal
 - (d) Transformer iron
15. Steel containing small quantities of elements such as Al , B , Cr , Co , Mo is called
 - (a) Alloy steel
 - (b) Stainless steel
 - (c) Plain carbon steel
 - (d) Mild steel
16. Steel with 20% Ni , 12% Al , and 6% Co used for making powerful electromagnets is
 - (a) Stainless steel
 - (b) Alnico
 - (c) Nichrome
 - (d) Monel metal

17. The following table gives the alloy with its composition. Which of the following is incorrect?
- | | |
|------------------|--|
| (a) Nickel steel | 25–28% Ni, 1–4% Mn, 0.5% Cr and 0.3–0.5% C |
| (b) Invar steels | 30–36% Ni, 0.3–0.5% C |
| (c) Platinite | 46% Ni and 0.15% C |
| (d) Parmolloy | 80% Ni and 20% C |
18. Steels which can absorb sudden shocks are called
- | | |
|-------------------|-----------------------|
| (a) Tool steels | (b) High speed steels |
| (c) Spring steels | (d) Low speed steels |
19. The composition of German silver is
- | |
|--|
| (a) Cu = 25–50%, Zn = 10–35%, Sn = 5–35% |
| (b) Cu = 10%, Zn = 5%, Sn = 25% |
| (c) Ni = 60%, Zn = 20%, Ag = 8% |
| (d) Cu = 25–30%, Zn = 2–5%, Sn = 4–8% |
20. An alloy of aluminium used extensively in aircraft industry as alclad is
- | | |
|----------------|---------------|
| (a) Magnalumin | (b) Duralumin |
| (c) Constantan | (d) Monel |
21. Which of the following is not the heat treatment process of steel?
- | | |
|---------------|-----------------|
| (a) Annealing | (b) Normalising |
| (c) Tempering | (d) Compacting |

Solutions

- | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (c) | 3 (c) | 4 (a) | 5 (b) | 6 (b) | 7 (c) |
| 8 (d) | 9 (b) | 10 (a) | 11 (d) | 12 (b) | 13 (d) | 14 (b) |
| 15 (a) | 16 (b) | 17 (d) | 18 (c) | 19 (a) | 20 (b) | 21 (d) |

Chapter 5

ENGINEERING MATERIALS

5.1 Cement

Introduction

Cement is a binder, a substance that sets and hardens independently, and can bind other materials together. It is used in construction for binding materials like bricks, stones and tiles, and is also used for flooring and plastering purposes.

Cements used in construction can be either *hydraulic* or *non-hydraulic*. *Hydraulic cements* (e.g., Portland cement) set and harden because of hydration and hydrolysis reactions between the anhydrous cement powder and water.

Non-hydraulic cement such as slaked limes (calcium hydroxide mixed with water) harden due to the carbonation reaction by carbon dioxide present naturally in the air.

Cement alone cannot be used for construction work. It is used as a mixture with sand and crushed stones. It may be used as mortar or concrete.

Mortar It is a mixture of cement, sand and water which is used for binding bricks together and for plastering.

Concrete It is a mixture of cement, gravel (crushed stones), sand and water. It is used in flooring works, columns, beams, foundations, etc. If instead of cement, lime is used, then the concrete is known as lime concrete.

Reinforced concrete construction (RCC) It is concrete reinforced with steel rods or heavy wire mesh. Reinforced concrete is used in floors, beams, girders, columns, slabs, bridges, etc. It imparts high tensile strength to structures.

Portland cement was discovered by Joseph Aspdin in 1824. The name Portland cement comes from the fact that the colour and quality of the resulting concrete are similar to Portland stone, a kind of limestone found in England.

Types of cements

The different types of cements based on Indian Standards are as follows:

1. **Ordinary Portland cement** It is the most important type of cement and is commonly called OPC. It is made by grinding and mixing clay and lime bearing minerals in proper proportions and then heating the mixture to nearly 1400 °C. It is not in much use these days, having been replaced by Portland pozzolana cement (PPC).
2. **Portland pozzolana cement** It can be fly ash-based or calcined clay-based. PPC is obtained by mixing OPC with suitable pozzolans at a certain temperature. Pozzolans are deposits of volcanic ash produced by rapid cooling. When mixed with slaked lime, pozzolans show properties similar to cement when it comes in contact with water. PPC is commonly used for various construction activities.
3. **Rapid hardening cement** As the name indicates, this cement hardens at a very rapid pace. Apart from rapid hardening, it also develops high strength earlier than OPC. It is used in pre-fabricated concrete construction works or at places where framework has to be removed for reuse at a fast rate. It is sometimes also used in road repair works.
4. **Sulphate resisting cement** OPC is vulnerable to the attack of sulphates, hence, as the name indicates, this type of cement is resistant to the attack of sulphate. It finds use in concreting done in marine conditions or in concrete foundations where the soil contains sulphate compounds. It is also used in sewage treatment works.
5. **Portland slag cement** This type of cement is made by mixing Portland cement and ground granulated blast slag in suitable proportions. The resultant cement is more resistant to chemical attacks. It is generally used in water retaining structures or where the structure is vulnerable to any form of chemical attack.
6. **Super sulphated cement** This cement is like sulphate resisting cement but with a higher percentage of granulated slag. It has higher sulphate resistance and fineness than OPC. It is used in foundation works (or sea works) where very high degree of sulphate resistance is required.
7. **Coloured cement** It is generally white in colour but can be turned to any colour by adding suitable coloured pigments in OPC or PPC. It is manufactured from limestone that is available only near Jodhpur in India. Coloured cement is used to enhance the beauty and appearance of various monuments.
8. **Hydrophobic cement** It is manufactured by grinding together OPC clinkers with substances such as oleic acid or stearic acid that are famous for their film forming nature. It reduces the rate of deterioration of cement and thus gives long storage life to cement.
9. **Masonry cement** It is used for masonry works and has properties resembling lime mortar instead of cement mortar. It is manufactured using certain admixtures.

10. **High alumina cement** It is cement with very high alumina content. High alumina cements have a high rate of hardening and develop good strength.

Manufacture of cement

Rotary kiln method

Portland cement is manufactured by mixing lime and clay. The raw materials used for the manufacture of Portland cement are given below.

- (i) **Calcareous materials** These materials supply lime, for example, limestone (contains 65%–80% CaCO_3), chalk, calcite and waste calcium carbonate from industrial processes.
- (ii) **Argillaceous materials** These materials supply silica, iron oxide and alumina, for example, clay, marl, shale, etc. All these materials should have 2.5 to 4 times more silica than alumina.
- (iii) **Gypsum** $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- (iv) Powdered coal as fuel.

The manufacture of Portland cement involves the mixing of calcareous and argillaceous substances in the required ratio. The mixture is heated to 1400 °C–1600 °C (fusion point). The clinkers so obtained are cooled, powdered and mixed with 2% to 5% gypsum. The various steps involved in the manufacture process are

- Mixing
- Burning
- Cooling
- Grinding
- Packing

1. *Mixing of raw materials*

The raw materials are ground and then mixed either by (a) dry process or (b) wet process

- a) **Dry process** The calcareous and argillaceous substances are ground separately without adding water. Each of these is stored in a separate hopper. The two are then mixed in the proper ratio by automatic weighing machines and then the dry powdered mixture (moisture 2%) is fed into the furnace.
- b) **Wet process** In this method the calcareous substances are ground dry and stored in silos. The argillaceous substances are washed to remove impurities and then ground. The calcareous and argillaceous substances are mixed in the presence of water (30%–40%) to get a free flowing slurry. The slurry is then led into the correcting basin where its chemical composition is adjusted to the proper ratio. The slurry is stored in big storage tanks before being fed into the furnace.

Table 5.1 provides a comparison between the wet and dry process.

Table 5.1 Comparison between wet and dry process

S.No	Dry process	Wet process
1	It is a slow process	It is relatively faster
2	Fuel consumption is low. Shorter kiln is required. Cost of cement production is less	More fuel is required to evaporate excess water. Longer kiln is needed for the same purpose. Cost of cement production is high
3	Causes environmental pollution as the raw materials are ground dry	Causes less environment pollution as grinding is done by adding water
4	The quality of cement produced is inferior	Cement produced is of better quality
5	The process is adopted when the raw materials are quite hard and cannot be disintegrated by water	This process is preferred for soft raw materials
6	This process is not suitable when the raw materials have an inherent moisture content of 15% or more	The process is used when the percentage of moisture in raw materials is high
7	Method is used in cold countries where water might freeze at low temperatures	Cannot be used in cold climatic conditions because the water will freeze

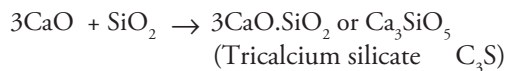
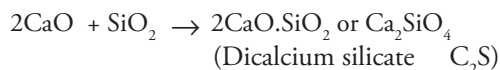
1. **Burning** Burning is usually done in a rotary kiln, which is a long steel cylinder (length: 90–120 m and diameter 2–4 m) lined with refractory bricks. It is slightly inclined towards the exit end and is mounted on rollers. It rotates gradually to enable proper mixing of the raw material (Fig. 5.1). The material is introduced in the kiln from the upper end. The kiln is heated by burning pulverised coal and the temperature is maintained at 1600 °C–1700 °C. The material introduced from the upper end moves downwards due to inclination and rotatory movement of the kiln. The various chemical reactions taking place are as follows.

- (a) **Drying zone** This is the upper one-fourth portion of the kiln where the temperature is 100–500 °C. This zone is known as the drying zone because all the moisture from the slurry is removed here. The dry material moves down the kiln.
- (b) **Calcination zone** It is the middle part of the kiln and the temperature here is about 1000 °C. All the organic matter burns here and calcium carbonate decomposes to form CaO and CO₂.



CO₂ escapes out and the material acquires the shape of lumps.

- (c) **Burning zone or clinkering zone** It is the hottest and lowermost portion of the kiln. The temperature here is 1400 °C–1600 °C. In this zone, the mixture melts, chemical reaction between lime and clay takes place forming calcium aluminates and silicates. The reactions taking place are given below.



These aluminates and silicates combine together to form small, round, greyish stones called clinkers.

- (b) **Cooling zone** The clinkers produced above are cooled by a stream of air and the hot air so produced is used for drying the coal before pulverisation.

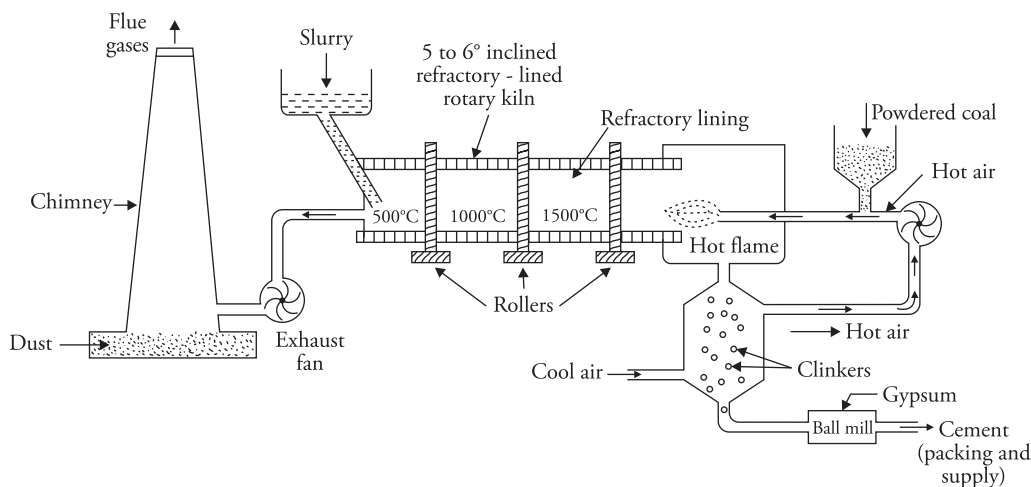
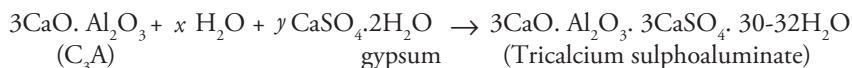


Figure 5.1 Line diagram of rotary kiln for the manufacture of cement

2. **Grinding** The cooled clinkers are ground in ball mill with the addition of 2%–5% gypsum. Finely ground clinkers set very quickly when they come in contact with water. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) acts as a retarding agent and delays this setting. When cement is mixed with water, the initial set takes place due to hydration of tricalcium aluminate. Gypsum

($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) reacts with tricalcium aluminate and retards its hydration forming insoluble tricalcium sulphaaluminate which does not hydrate quickly.



3. **Packing and supply** The cement coming out of the grinding mill is stored in concrete storage called silos. Moisture free air is used to agitate the cement and keep it free from compaction. The cement is packed in bags by automatic packing machines.

The flow diagram for the manufacture of cement by the rotary kiln method is shown in Figure 5.2.

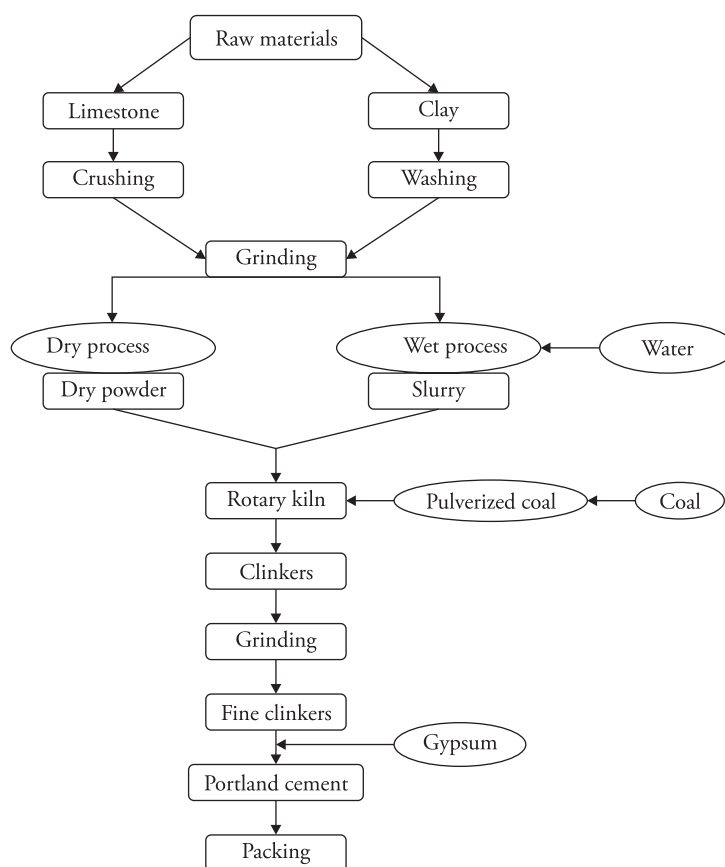


Figure 5.2 Flow diagram for the manufacture of cement by the rotary kiln method

Vertical shaft kiln method

Rotary kilns are used in large cement plants capable of big investments. However, the vertical shaft kiln (VSK) method can be used in mini cement plants with a capacity of 40,000–150,000 tons

per annum. In this method, the kiln is vertical instead of inclined (as in the rotary kiln). In VSK technology, fuel is mixed with raw materials in the proper ratio by a pan noduliser or pelletiser. This is done in two ways.

- (i) Black meal process
- (ii) Fuel slurry process

Black meal process The raw materials are ground with coal in the calculated proportion. Since the ground raw material is black in colour, the process is called 'black meal process'. This powdered material is then converted into pellets by adding 15% water.

Fuel slurry process In this process, dry raw materials are ground in a tube mill or roller mill. Coal is ground wet separately with equal amount of water. The dry powdered raw materials and coal slurry are mixed properly and converted into pellets in a pelletiser.

Process The pellets made by any of the process (black meal or fuel slurry process) are fed into the VSK through a hopper. The kiln is lined with refractory bricks. As the pellets move downwards, they are heated and sintered by the ascending hot gases. The sintered pellets so formed are discharged from the bottom of kiln through a slowly rotating grate (Fig. 5.3).

The various zones of reaction starting from the top of the kiln are:

- (i) **Preheating zone** Here the temperature is 100 °C–500 °C. All the moisture is removed from the pellets.
- (ii) **Calcination zone** Temperature here is about 1000 °C. The decomposition of CaCO_3 takes place.
- (iii) **Sintering zone** Temperature in this region is about 1400 °C–1600 °C. Various chemical reactions leading to the formation of clinkers take place (*for reactions please refer to the section on rotary kiln method*)
- (iv) **Cooling zone** The clinkers are cooled with a blast of cold air. The air gets heated in cooling the clinkers and is utilised in combustion of the coal present in clinkers. The clinkers are finally extracted from the bottom of the kiln and ground with 4%–5% gypsum before packing.

Advantages of vertical shaft kiln technology

1. Due to the use of pellets, dust is not discharged into the atmosphere.
2. Due to control over the shape of clinkers, it reduces the wear of grinding machinery. The cost of grinding is reduced.
3. Low melting constituents are not formed, and thus there is no problem of clinkers clogging the refractory lining in the heat zone. It saves labour, reduces consumption of refractories and increases production.
4. The kiln is usually 10 m tall and hence the plant is quite compact.
5. It has lower maintenance cost and requires less capital investment.

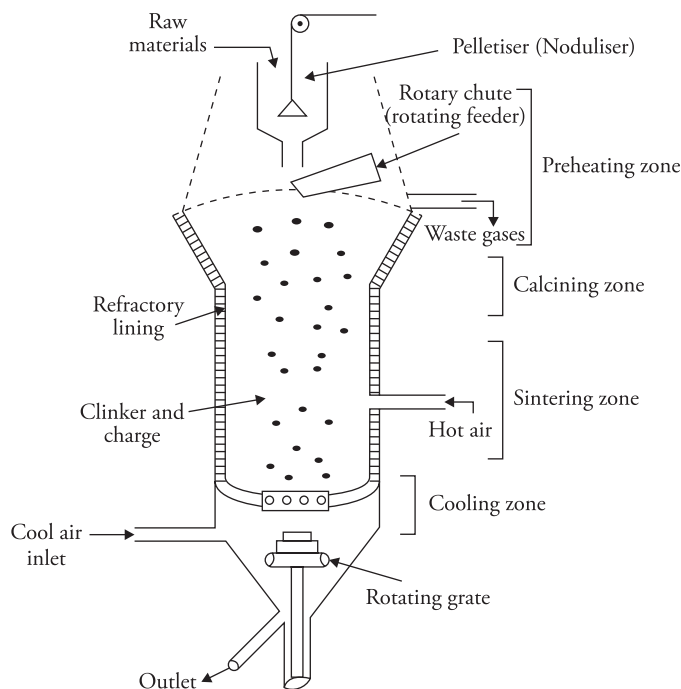


Figure 5.3 Vertical shaft kiln

Chemical composition of cement

Abbreviations used

$\text{CaO} = \text{C}$, $\text{SiO}_2 = \text{S}$, $\text{Al}_2\text{O}_3 = \text{A}$, $\text{Fe}_2\text{O}_3 = \text{F}$, $\text{Ca}(\text{OH})_2 = \text{CH}$,

$\text{H}_2\text{O} = \text{H}$, $\text{SO}_3 = \text{S}$ (sulphur trioxide)

Thus, we can write $3\text{CaO} = \text{C}_3$ and $2\text{CaO} \cdot \text{SiO}_2 = \text{C}_2\text{S}$.

The properties of cement depend upon the relative proportions of the components present. The properties can be modified by varying the amount of these constituents. Table 5.2 lists the main constituents of Portland cement.

Table 5.2 Main constituents of Portland cement

Name of the compound	Chemical formula	Abbreviation used	Average %	Setting time
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S	45	7 days
Dicalcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S	25	28 days
Tricalcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A	1	1 day
Tetracalcium aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF	9	1 day

Apart from the compounds mentioned in Table 5.2, some free CaO and MgO may also be present. The characteristics of the main constituents are given below.

- (i) *Tricalcium silicate* (C_3S): It has medium rate of hydration. It develops high ultimate strength rapidly. The heat of hydration is about 880 kJ/kg.
- (ii) *Dicalcium silicate* (C_2S): Its ultimate strength is quite comparable to C_3S but is slightly less. It hydrates very slowly and is also responsible for ultimate strength. It possess a heat of hydration of about 420 kJ/kg.
- (iii) *Tricalcium aluminate* (C_3A): It undergoes hydration at a very fast rate. The initial set or flash set of cement is due to C_3A . Its early strength is good but ultimate strength is poor.
- (iv) *Tetracalcium aluminoferrite* (C_4AF): It has slow rate of hydration. Both its early and ultimate strength are poor and hence do not contribute much to the strength of cement.

The proportion of the above constituents varies in different Portland cements. For example, if the clay used is free of iron, then C_4AF is absent and the cement is white. In addition to the above, free lime, ferric oxide and magnesium oxide are also present in Portland cement, but they have no effect on the properties of cement.

ISI specification of Portland cement

The ISI specifications of Portland cement are as follows.

- (i) Ratio of the percentage of lime (CaO) to that of silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) should not be more than 1.02 and not less than 0.66 when calculated by the formula:

$$\frac{CaO - 0.7 SO_3}{2.8 SiO_2 + 1.2 Al_2O_3 + 0.65 Fe_2O_3}$$

- (ii) Ratio of the percentage of alumina (Al_2O_3) to that of iron oxide (Fe_2O_3) should not be less than 0.66

$$\frac{Al_2O_3}{Fe_2O_3} \geq 0.66$$

- (iii) The weight of the insoluble residue should not exceed 2%.
- (iv) Weight of magnesia (MgO) should not exceed 6%.
- (v) Total sulphur contents, calculated as SO_3 , should not be more than 2.75%.
- (vi) Total loss on ignition should not be more than 4%.

Great care should be taken to see that the composition of cement satisfies the above parameters because

- (a) If *too much* lime is present, the cement will be 'unsound', that is, after some time; concrete made from it will expand and crack.
- (b) If lime is *too little*, the concrete will be low in strength and may 'set quickly', that is, harden even before the mason places it.

- (c) Cement with *high alumina* content also sets fast.
- (d) *High silica* cement hardens very slowly and does not attain full strength for a long period.

Requirements of cement

1. **Setting time** *Initial* – Not less than 30 min; *Final* – Not more than 600 min.
2. **Compressive strength** 1:3 cement mortar cube of cement and Ennore sand
3 days: Not less than 1.6 kg/mm² (or 16 N/mm²)
7 days: Not less than 22 kg/mm² (or 22 N/mm²)
3. **Soundness** It expresses the expansivity of the cement set in 24 hours between 25 °C and 100 °C. For aerated cement, it should be maximum 5 mm and for unaerated cement, it should be maximum 10 mm. If a cement on hydration produces very small change in volume, it is said to be 'sound'. In Le Chatelier's test, a test piece of specific dimensions is placed in boiling water for 3–5 hours and its expansion is measured.
4. **Fineness** Not less than 215 m²/kg. The finer the cement, the faster is the rate of reaction and hence, strength develops early. However, fine cement generates heat quickly and thereby, cement mortar/concrete is likely to develop cracks.
5. **Specific gravity** Should be 3.1 to 3.2.
6. **Tensile strength** Not less than 300 lbs/sq inch after 72 hours.

The approximate composition of Indian Portland cement is tabulated below.

Constituent	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	Losses
Percentage	23%	2.19%	5.97%	64.86%	1.0%	1.75%	0.74%

Setting and hardening of cement

When cement is mixed with water and allowed to stand, it changes to a hard rigid mass. This is known as setting. Setting refers to a change from a fluid state to a rigid state due to initial gel formation.

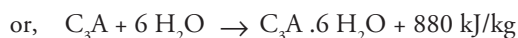
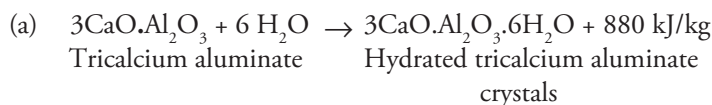
Gradually, the rigid mass gains strength to form a compact rock-like material. This development of strength due to crystallisation is called hardening.

Setting and hardening takes place due to *hydration* and *hydrolysis* reactions of the various constituents of cement. The hydrated compounds being less soluble, precipitate out as gels or crystals. These insoluble gels surround inert materials like sand or crushed stones (in mortars or concrete) and bind them strongly. It is believed that hardening takes place due to interlocking of the crystalline products formed during hydration.

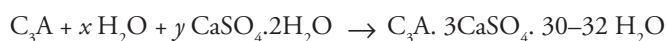
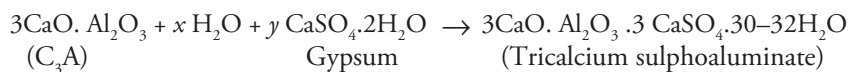
Setting occurs within 24 hours, whereas hardening requires 15 to 30 days. It is believed that the setting times of C₃A, C₄AF, C₃S and C₂S are 1 day, 1 day, 7 days and 28 days, respectively.

The chemical reactions taking place during setting and hardening are as follows.

- (i) **Initial setting** Initial setting refers to the beginning of the cement paste setting. When cement is mixed with water, the paste becomes stiff immediately. This immediate stiffening after mixing, making proper placing and finishing impossible is called '*flash set*'. It is due to hydration of tricalcium aluminate (C₃A). It is accompanied by evolution of considerable heat.

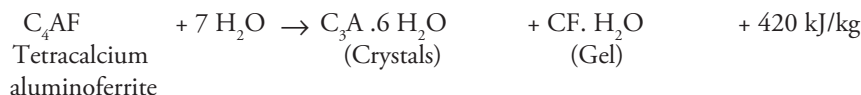


Flash set is not desirable as it causes loss of workability of cement and prevents hydration of the other constituents of cement. Gypsum is added to retard flash set or initial set.

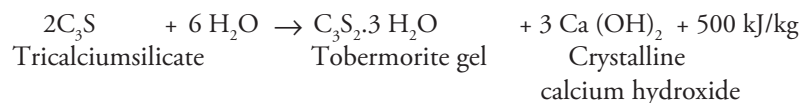


Gypsum reacts with C_3A forming insoluble tricalcium sulfoaluminate, which does not hydrate rapidly.

b) Tetracalcium aluminoferrite also undergoes hydrolysis forming crystalline products.

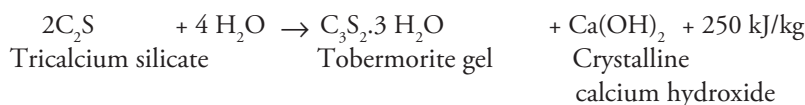
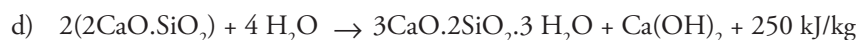


c) Hydration of C_2S also starts within 24 hours and is completed in 7 days.



(ii) **Final setting and hardening**

It refers to the beginning of hardening and gain of strength. Final setting starts after ~10 h and continues for several months. Hydration of dicalcium silicate occurs slowly between 7 to 28 days.



Tobermorite gel serves as a bonding material between cement particles. It is the main component that gives strength to cement. $\text{Ca}(\text{OH})_2$ does not contribute to strength but brings the pH value above 12 and is good for corrosion protection of steel.

As the hydrolysis and crystallisation proceed, the strength and hardness of cement increases. The process takes nearly 28 days.

The whole process can be schematically represented as in Figure 5.4.

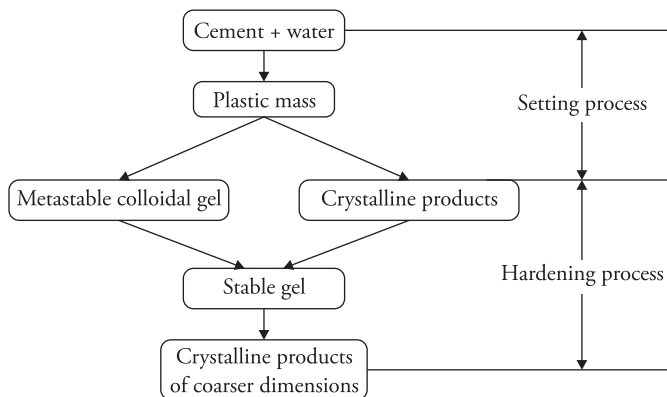


Figure 5.4 Schematic representation of setting and hardening of cement

5.2 Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

Gypsum is a naturally occurring mineral found in association with sedimentary rocks. It is generally associated with impurities like clay, calcium, magnesium, carbonates and iron oxide.

Synthetic gypsum is recovered via flue gas desulphurisation of some coal fired power plants.

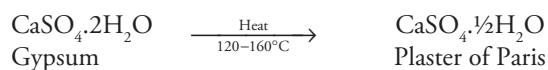
Properties It is a colourless, transparent or translucent crystalline mineral. It can also be white, grey, red, brown or yellow in colour. Gypsum is very soft and can be scratched by fingernail. It has low thermal conductivity. It is a natural insulator.

Uses Gypsum is primarily used for the production of plaster of paris. About three-fourth of its total production is calcined for this use. It is also used as a retarder in Portland cement. Crude gypsum is used as a fluxing agent, soil conditioner, filler in paper and textiles. Gypsum is also used as a building material in plaster, board products, tiles, blocks, manufacture of some cement. It also finds use in the manufacture of fertilizers.

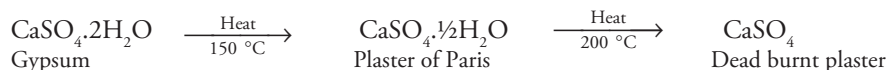
5.3 Plaster of Paris ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ or $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)

Preparation

Plaster of Paris is prepared by heating gypsum to a temperature of 120°C – 160°C .

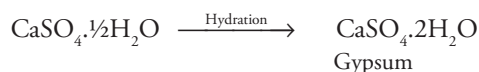


If the temperature rises above 200 °C, all the water is lost resulting in the formation of anhydrous salt called *dead burnt plaster*. It has no setting properties.



During the preparation of plaster of paris, gypsum is crushed, ground and then calcined in kilns at about 150 °C to produce a product which is pulverised to yield plaster of paris.

Properties It is a white powder which on mixing with water forms a plastic mass. The plastic mass sets into a hard solid in 5–10 min. This is called setting of plaster of paris. The setting is due to hydration of plaster of paris to form gypsum.

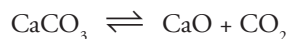


During setting, there is a slight increase in volume. This helps plaster of paris to take the shape of the mould in which it is placed. The rate of setting is increased by adding accelerators like alkali sulphates K_2SO_4 , Na_2SO_4 (or alums), which initiate as well as hasten the crystallisation process.

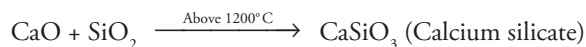
Uses Plaster of paris is used for producing moulds for plastics, ceramics, etc. It is also used for plastering walls, for making statues, moulds and other decorative items. Besides this, plaster of paris also finds use in surgical bandages known as ‘plaster’ for setting broken and fractured bones in the body.

5.4 Lime

Lime is also used as a cementing material. Chemically, it is calcium oxide and is prepared on a commercial scale by heating limestone (CaCO_3) in a special type of rotary kiln at about 895 °C.

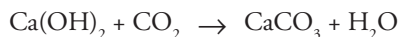
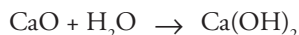


The temperature should not be allowed to rise above 1200 °C otherwise silica (SiO_2) present as impurity in limestone will react with calcium oxide to form calcium silicate.



Properties Lime paste shrinks and cracks, hence it is not a satisfactory cementing material. Lime mortar is a mixture of lime, water and sand. It is used to secure bricks, blocks and stone together. The setting of lime mortar takes place as follows.

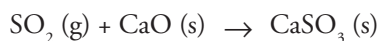
First, the water is lost from lime mortar either due to evaporation or absorption of water by porous bricks and this stiffened mass then absorbs CO_2 on exposure to air and is gradually converted to CaCO_3 .



The CaCO_3 crystals interlock with the sand particles and this leads to gradual hardening. Hardening is a very slow process and takes months and years for completion.

Uses

- Lime is used in iron and steel industry to remove silica impurity. It reacts with silica to form silicates (slag). The slag is then drained out.
- Lime is used for pollution control. It is used in the gas scrubber to reduce SO_2 emissions from power plants.



- Lime is added to sewage to remove phosphates.
- $3\text{CaO} + 3\text{H}_2\text{O} + 2\text{PO}_4^{3-} (\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2 (\text{s}) + 6\text{OH}^- (\text{aq})$
- It is used for water softening (lime–soda process)
- Being highly alkaline, it is used in the paper industry for pulping. It dissolves lignin that binds the fibers' together.
- Mixture of lime, sand and gravel was widely used in construction activities prior to the discovery of Portland cement.

5.5 Glass

Introduction

Glass is an amorphous, hard, brittle, transparent or translucent, supercooled liquid of infinitely high viscosity.

Chemically, glass is a fused mixture of silicates of alkali and alkaline earth compounds and other constituents like CaO , MgO , barium oxide, lead oxide, etc. It does not have a definite chemical composition. However, it may be represented as



where x and y are whole numbers

R is a monovalent alkali metal like Na, K, etc.

M is a bivalent metal atom like Pb, Ca, and Zn.

Ordinary glass, soda lime glass is represented as $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$.

Properties of glass

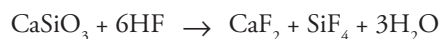
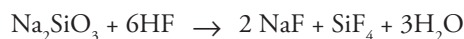
Physical properties

1. It is an amorphous, non-crystalline, generally transparent solid insoluble in water.

2. It is hard and has no definite melting point. On heating, it gradually softens and changes into a viscous liquid.
3. It is a bad conductor of heat and electricity.
4. It is brittle and breaks in an irregular manner by mechanical jerks or vibrations.
5. It has high viscosity (greater than 10^{13} poise).
6. It can incorporate colouring matter preserving its transparency.
7. Glass is a vitrified (non-crystalline) product. However, if the glass is cooled slowly, it undergoes crystallisation on the surface. This phenomenon is called devitrification.

Chemical properties

1. Glass is inert to all acids. Only HF reacts with silicates present in the glass.



2. Ordinary glass is readily attacked by alkalies.
3. It is not attacked by air or oxidising agents.

Devitrification

Under certain conditions, glass becomes ‘contaminated’ with crystalline particles. A glass in this condition is termed ‘devitrified’, which means that it has partially or completely crystallised. Devitrified glass, unless of the very special variety that is deliberately produced, is undesirable since the crystalline areas are extremely weak and brittle. The areas on the surface of devitrified glass are not glossy and have a hazy appearance. The glass seems to have a white coating that appears to be part of glass itself and cannot be removed by scrubbing or washing.

Causes of devitrification

- *Inadequate cleaning of glass* Presence of fingerprints, foreign residue, dust.
- *Firing too hot and too long* If the glass stays at a temperature above 1300 °F for too long, it becomes prone to devitrification.
- *Presence of chemicals* Usually the darker and more opaque the glass, the more chemicals it has and the greater are the chances of devitrification. Clear or uncoloured glasses are less likely to devitrify. Devitrification is common in glass that has high lime content.
- The presence of dust and debris in the kiln where the glass is produced leads to devitrification.

Prevention of devitrification

1. Glass surface should be clean.
2. Glass with high lime content should not be used.
3. Kiln should be free from dust.
4. Glass should spend less time at high temperature.
5. A devit spray like borax can be applied to the surface of the glass before firing.

Manufacture of glass

Raw materials

- a) Soda, Na_2CO_3 (soft glass)
- b) Potash K_2CO_3 (hard glass)
- c) Limestone, chalk
- d) Litharge or red lead (flint glass)
- e) Quartz, white sand for silica
- f) Zinc oxide (heat and shock proof glass)
- g) Borax and boric acid (heat and shock proof glass)
- h) Culletts or pieces of broken glass to increase fusibility
- i) Colouring agents: Yellow – Ferric salt; Green – Ferrous and chromium salts; Blue – Cobalt salts; Red – Nickel salts or Cu_2O ; Purple – MnO_2 , etc.

Functions of different constituents of glass

- i) K_2O : Increases the softening point
- ii) Fe_2O_3 : Prevents the transmission of UV light in glass
- iii) PbO : Increases the refractive index of glass
- iv) B_2O_3 : Increases the hardness of glass and lowers its thermal coefficient of expansion

Manufacturing process

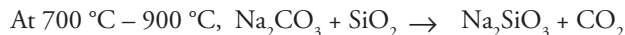
The manufacturing process (Fig. 5.5) can be divided into four steps:

- i) Melting
- ii) Forming and shaping
- iii) Annealing
- iv) Finishing

Melting Raw materials like limestone, silica, soda ash is finely powdered and mixed with cullets. This mixture of raw materials called 'batch' is blended in a rotary mixer to obtain an even mixture of ingredients and fed into the furnace. It is then fused either in a pot furnace or in a tank furnace in which heating is done by burning producer gas and air over a mixture of charge. The charge melts and fuses at a high temperature of about 1800°C . CO_2 is evolved. When all the CO_2 has escaped, decolourisers (such as MnO_2 or nitre) are added to remove ferrous compounds and carbon if present. If coloured glass is desired, then colouring agents are added at this stage. Heating is continued till the molten mass is free from bubbles, it is then cooled to about 800°C . The reactions taking place are given below.

- (a) **For soda glass (soft glass) (batch: Na_2CO_3 , CaCO_3 , SiO_2)**

At $< 600^\circ\text{C}$, moisture and small amounts of oxides of As, Sb, Pb, B and chlorides of Na, K, Fe, Sn, etc. are evaporated.



(b) **For flint glass (batch: Pb_3O_4 , K_2CO_3 , SiO_2)**



(ii) **Forming and shaping** Molten glass is then moulded into desired shapes.

(iii) **Annealing** The manufactured glass articles are cooled very slowly. This process of slow cooling which is used to reduce the strain is called annealing.

Since glass is a bad conductor of heat, by rapid cooling, the outer surface cools more quickly than the inner one. The unequal cooling results in strain and the glass is likely to crack into pieces. To avoid this, glass must be cooled gradually.

(vi) **Finishing** After annealing, the glass articles are subjected to cleaning, grinding, polishing, cutting, and sand blasting.

The flow chart of the manufacture of glass is shown in Figure 5.6.

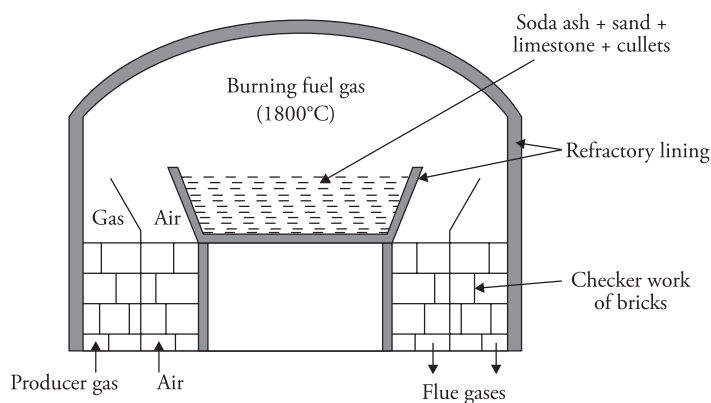


Figure 5.5 Manufacture of glass (tank furnace)

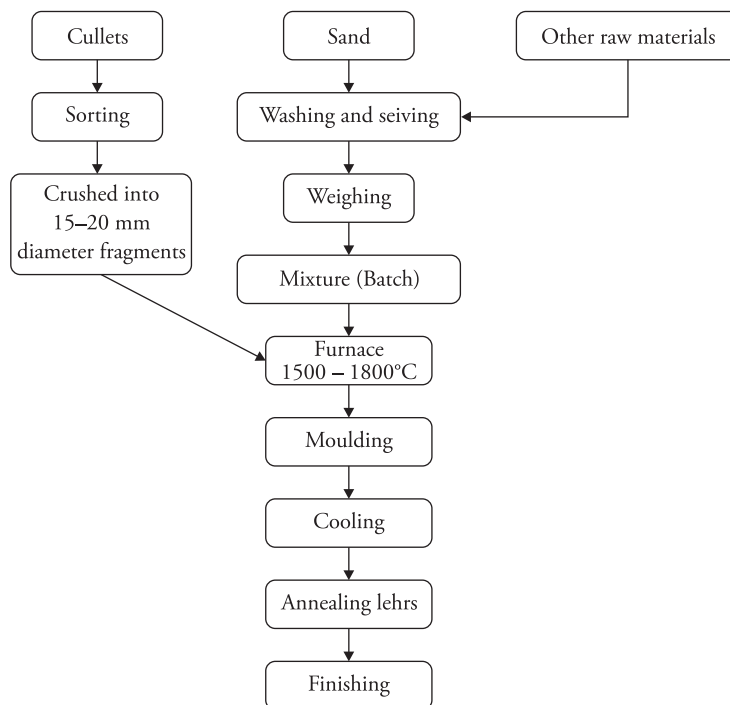


Figure 5.6 • *Flow chart of manufacture of glass*

Importance of annealing

The process of slow cooling of glass, which is used to reduce the strain, is known as annealing.

During manufacturing, if the glass is cooled rapidly, the outer surfaces cool more than the inner ones. Unequal cooling results in strain. Such a glass is likely to crack or break; it cannot withstand change of temperature or shock.

Annealing is carried out in annealing lehrs or annealing chambers.

Annealing lehr This consists of a tunnel 20–25 m long and 1–3 m wide in which trolleys carrying glassware move from hot to cold end (Fig. 5.7). Lehrs are heated at one end either directly or electrically.

Annealing chambers Here the glasswares are stacked and the chamber is heated up and then gradually cooled by closing it from all sides (Fig. 5.8).

In annealing, the manufactured glass article is kept above its critical temperature and then cooled slowly so that the internal strain is removed. Glass articles thus produced can withstand shock and temperature variations.

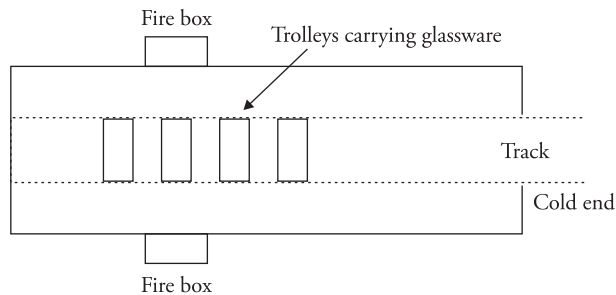


Figure 5.7 Annealing lehrs

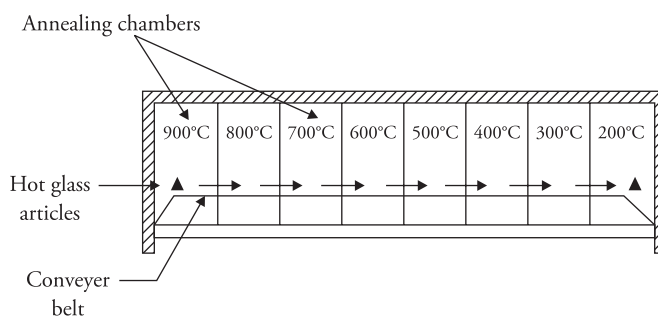


Figure 5.8 Annealing chamber

Types of glasses

Depending on their composition, there can be a large variety of glasses. Some of the major types are given below.

1. Soda glass or soft glass

It is the simplest variety of glass. Nearly 90% of the present day glass belongs to this category.

Approximate composition $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$

Preparation It is obtained by fusing together sodium carbonate, calcium carbonate and SiO_2 . The carbonates decompose to oxides on heating.

Properties

- It is low in cost.
- It is resistant to devitrification and is relatively resistant to water.
- It has low melting point and thus can be worked easily.
- It has limited chemical stability, and is attacked by common reagents like acids.
- It melts easily and hence cannot be used at high temperature.

Uses

- a) Glass containers, flat glass, electric bulbs and fluorescent tubing
- b) Cheap tableware like bottles, jars, etc.
- c) Cheap laboratory apparatus

2. Potash glass or hard glass

Approximate composition $K_2O \cdot CaO \cdot 6SiO_2$

Preparation It is obtained by fusing together potassium carbonate, calcium carbonate and SiO_2 .

Properties

- a) It possesses high melting point.
- b) It fuses with difficulty.
- c) It is more resistant to acids, alkalis and other solvents.
- d) Costlier than soda lime glass.

Uses

- a) Used for preparing chemical apparatus, combustion tubes, etc., which are to be used for heating operations.

3. Lead glass or flint glass

Approximate composition $K_2O \cdot PbO \cdot 6SiO_2$; as much as 80% PbO is incorporated for dense optical glasses.

Preparation It is obtained by fusing together potassium carbonate, red lead and silica.

Properties

- a) It is heavy, shining and very durable.
- b) Its softening temperature is lower than soda glass, but it is much easier to shape and work with.
- c) It has high refractive index.
- d) Its specific gravity is high (3 to 3.3).

Uses

- a) Manufacture of high quality tableware and art objects, cut glass articles (decoration articles, imitation diamonds or jewels) because of its high lustre.
- b) Making optical instruments like prisms and lenses.
- c) Leaded glasses containing as much as 92% PbO (called flint glass) are used for windows and shields to protect personnel from gamma rays and X-rays in medical and atomic energy fields, respectively.

4. Borosilicate glass or Pyrex glass or Jena glass

Approximate composition

Component	SiO_2	B_2O_3	Al_2O_3	K_2O	Na_2O
%	80.5	13	3	3	0.5

In borosilicate glass, B_2O_3 is used instead of lime. Sometimes, ZnO may be added to improve its properties.

Preparation

It is obtained by fusing a mixture of sand, lime, borax and alkali metal carbonates.

Properties

- a) High chemical resistance.
- b) Low thermal coefficient of expansion.
- c) High softening temperature.
- d) Excellent shock resistance (shock proof).

Uses

Borosilicate glass is widely used for

- a) Superior quality laboratory glassware like flasks, test tubes, boiling tubes, beakers, etc.
- b) Kitchenware, glassware for use in microwave oven.
- c) In industry as pipelines for corrosive liquids.
- d) Television tubes, electrical insulators.

5. Aluminosilicate glass

Approximate composition

Component	SiO_2	Al_2O_3	B_2O_3	MgO	CaO	Na_2O+K_2O
%	55	23	7	9	5	1

Compared to borosilicate glass, this glass has a higher percentage of Al_2O_3 and lower percentage of B_2O_3 .

Properties

It possesses exceptionally high softening temperature.

Uses

- a) For high-pressure mercury discharge tubes
- b) For chemical combustion tubes
- c) For certain domestic equipment, etc.

6. Optical or Crook's glass or phosphate glass

It contains phosphorus oxide (P_2O_5) instead of SiO_2 and lead silicate, together with little cerium oxide.

Properties

- a) Have low melting point and are relatively soft.
- b) Low viscosity so that it becomes free of bubbles in molten state.
- c) Absence of impurities like iron and thus is colourless.
- d) No devitrification even on long annealing.
- e) Ability to take up the desired polish on grinding and polishing.

Uses

- a) They have high refractive index and are used for the manufacture of lenses.
- b) Crook's glass is a special kind of optical glass containing little CeO_2 and is capable of absorbing ultraviolet rays which are harmful to the eyes.

7. Safety glass or laminated glass***Preparation***

It is made by pressing two or more sheets of glass with one or more alternating layers of bonding materials like vinyl plastic or synthetic rubber. It is then heated till the glass layers and plastic layers merge into one another to give a sandwich like structure. On cooling, the glass becomes tough.

Properties

- a) It is quite tough.
- b) It is as strong as steel and three times lighter than steel.
- c) It is shatter proof (when it breaks, the pieces do not fly apart because the inner plastic layers hold them together).

Uses

- a) Used as wind shield in automobile and aeroplane industry (three-layered laminated glass).
- b) A five layered laminated glass is used in building construction.
- c) Several layers of glass with vinyl plastic resin in alternate layers is used for making bullet proof glass. Ordinarily, thickness of this glass varies from 12.7 mm to 76.5 mm.

8. Toughened glass***Preparation***

After conversion of glass articles into their desired shape, the hot articles are dipped in oil bath so that some chilling takes place. By doing so, the outer layers shrink and acquire a state of compression; while the inner layers are in a state of tension.

Properties

- a) Such a glass is more elastic and capable of withstanding mechanical and thermal shocks.
- b) When this glass breaks, it is reduced to fine powder and the broken pieces do not fly apart.

Uses

Toughened glass is used for making

- a) Window shields of trucks, cars, aeroplanes and other fast moving vehicles.
- b) Automatic opening doors.
- c) Large show cases.
- d) Car windshields and windows.
- e) Glass sliding doors and partitions in houses and offices.
- f) Glass furniture such as table tops.

9. Wired glass

Preparation

A wire mesh is embedded in the centre of the glass sheet during casting.

Properties

Wired glass is

- a) Shatter proof as the wire holds the broken pieces together.
- b) More fire resistant than ordinary glass.

Uses

Used for making fire resistant doors, roofs, windows and sky lights.

10. Glass wool

It is a fibrous wool-like form of glass. It is composed of intermingled fine filaments of glass.

Preparation

It is prepared by forcing molten mass of glass through small holes of average diameter 0.005–0.007 mm continuously. The glass fibres so obtained are thrown over a rapidly revolving drum to get the material in the form of wool.

Properties

- a) Non-combustible, fire proof and heat proof.
- b) Thermal and electrical conductivity is low.
- c) Its tensile strength is about eight times that of steel.
- d) It is resistant to moisture and chemicals.
- e) Its density is quite low (about 65 kg/m³).

Uses

- a) For the filtration of acidic and corrosive liquids.
- b) In domestic and industrial appliances like oven, insulation of metal pipelines, motors, vacuum-cleaners, etc., where heat insulation is required.
- c) For sound and electrical insulation.
- d) For making costumes of fire-men.

11. 99.5% Silica glass or vitreosil

Preparation and properties

It is produced by heating pure sand (SiO₂) to its melting point (about 1750 °C). As fluxing agents are absent, it is extremely difficult to get rid of air bubbles. Moreover, due to high viscosity of this glass at its working temperature, shaping is rather difficult. The final product is translucent. Its softening temperature is about 1650 °C and the thermal coefficient of expansion is the lowest.

If vitreosil glass is heated for long periods above its melting point, it finally becomes transparent and then it is known as 'clear silica glass'. It has considerable light transmission properties – 1-m-thick material allows about 93% of light to pass through.

Uses

- a) Mainly for chemical plants.
- b) In chemical laboratory wares.
- c) As electrical insulating materials in electrical heaters, furnaces, etc.

12. Polycrystalline glass or Pyroceram***Preparation***

It is produced by adding one or more nucleating agents to the conventional glass batch, which is then moulded into desired shape. The material is then subjected to controlled heat treatment. The nucleating agents induce the formation of a large number of microscopic crystallites, which act as centres for further crystal growth.

Properties

- a) Crystalline glass is not ductile.
- b) Its impact strength is much greater than ordinary glass.
- c) It exhibits high strength and considerable hardness and can be formed and shaped into articles by moulding.

13. Neutral glass

This includes glasses which are highly resistant to chemical attack and are used in the manufacture of syringes. Neutral glasses can be regarded as specialised soda lime glass, in which some useful alkali has been replaced by alumina, boron oxide and other constituents.

14. Photochromatic glass

It contains a large number of microscopic particles of silver halide. On exposure to light, temporary colour centres consisting of silver particles are produced and these add up quickly producing darkness. The intensity of darkness depends on the concentration of silver. Since the reversible darkening is controlled by radiations in the UV region, photo blackening does not take place in lamp light at night.

15. Insulating glass

It is a transparent unit prepared by using two or more plates of glass separated by 6- to 13-mm-thick gap, filled with dehydrated air and then sealed around the edges. This provides a high insulation against heat. Thus if such a glass is used for apartments, it does not transmit heat and consequently apartments will remain cool during summer and warm during winter.

5.6 Refractories

Introduction

Refractories are inorganic, non-metallic materials that can withstand high temperatures without undergoing physicochemical changes while remaining in contact with molten slag, metals and gases. They are mostly used in lining of furnaces, kilns, crucibles, etc., which are generally heated to a very high temperature.

Characteristics of a good refractory

A good refractory should possess the following characteristics.

- It should be chemically inert to the corrosive action of gases, liquids and slags.
- Its physical, chemical and mechanical properties should not undergo substantial changes at high temperature.
- Its fusion temperature should be high.
- It should be resistant to the abrasive action of flue gases, molten metals, etc.
- It should not undergo cracking or deformation due to non-uniform expansion or contraction.
- It should not contaminate the material with which it is in contact.

5.6.3 Classification of refractories

Refractories can be classified based on

- Chemical composition
- Fusion temperature ranges
- Oxide content

Based on chemical composition On the basis of chemical composition, refractories are of three types

- Acid refractories* They are those which consist of acidic materials like silica and aluminium silicate. They are not attacked by acidic materials but are generally attacked by basic materials, for example, silica, alumina and fireclay refractories. Steel industries are the biggest consumer of silica refractories.
- Basic refractories* They are made of basic materials like CaO, MgO, etc. They are not attacked by basic or neutral media but are easily attacked by acidic materials, for example, magnesite, dolomite, chrome–magnesite refractories.
- Neutral refractories* They are not attacked neither by acidic nor by basic materials, hence they constitute the most satisfactory furnace lining. Examples of neutral refractories include graphite, chromite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$), zirconia (ZrO_2) and carborundum (SiC).

Based on oxide content:

- Single oxide refractories* Examples include alumina, magnesia and zirconia.
- Mixed oxide refractories* Examples include spinel, mullite.
- Non oxide refractories* Examples include carbides, nitrides, silicides and borides.

Based on temperature range of fusion On this basis, refractories are classified as given below.

Refractory	Fusion range	Example
Low refractory	1600–1800 °C	Fireclay refractory
High refractory	1800–2000 °C	Chromite refractory
Super refractory	> 2000 °C	Zirconia refractory

Properties of refractories

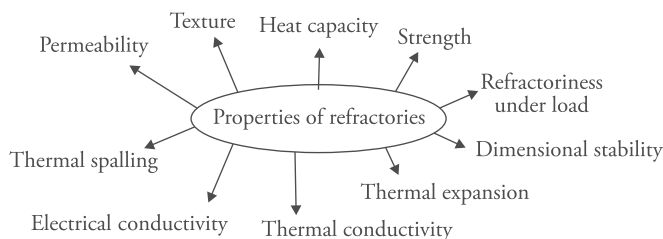


Figure 5.9 *Properties of refractories*

Refractoriness Refractoriness is the ability of a material to withstand high temperature without appreciable deformation or softening. It is generally measured by the softening or fusion temperature of the material.

A refractory material should have a softening temperature (refractoriness) higher than the operating temperature of the furnace.

Measurement of refractoriness (Seger cone test): As a refractory material is a mixture of several oxides, they do not have a sharp fusion temperature. Refractoriness is determined by the pyrometric cone test or the seger cone test. It is expressed in terms of pyrometric cone equivalent (PCE).

To determine refractoriness, standard cones called seger cones or pyrometric cones are taken. These cones have a fixed dimension (38 mm high and 19 mm base). They are assigned serial numbers and their fusion temperatures are determined (Table 5.3). Now the test refractory is given the shape of a cone with the standard dimensions (38 mm high and 19 mm base). The test cone is placed along with the seger cones and all are heated at a uniform rate (10 °C per minute). When the test cone softens one of the standard cones will also soften. When the apex of the test cone touches the base, the apex of some standard cone will also touch the base. This is the PCE value of the test cone. For example, if the test cone softens along with the seger cone No. 33, then the PCE value of the test cone is 33 and the softening temperature is 1700 °C–1750 °C. If more than one seger cone softens along with the test cone then the PCE value of the test sample is taken as the average of the two (Fig. 5.10).

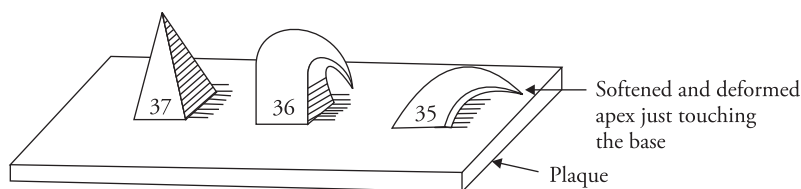


Figure 5.10 *Seger cone test*

Table 5.3 Seger cone number and fusion temperature

Seger cone number	Fusion temperature (°C)	Seger cone number	Fusion temperature (°C)
1	1110	12	1350
2	1120	13	1380
3	1140	14	1410
4	1160	15	1435
5	1180	16	1460
6	1200	17	1480
7	1230	18	1500
8	1250	19	1520
9	1280	20	1530
10	1300	21	1550
11	1320	22	1580

Strength /refractoriness under load Refractories used inside the furnace have to withstand high pressure and the load of the charge inside the furnace. Cold strength does not have much relation to the strength at higher temperatures. For example, fireclay refractories soften over a range of temperature but under conditions of heavy load, they soften far below their true fusion temperatures as determined by the seger cone test.

A better test for determining strength of a refractory inside a furnace is the RUL (refractoriness under load) test. RUL test is performed by heating a refractory specimen of size 5 cm² and 75 cm high under a constant load of 3.5 to 1.75 kg/cm²

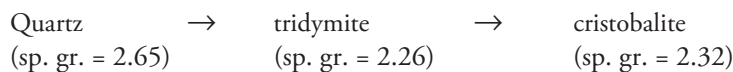
It is heated in a carbon resistance furnace at a standard rate of 10 °C/minute. A curve for temperature against height of the cone is plotted. RUL is reported as the temperature at which 10% deformation occurs on the test specimen. On the basis of RUL test, the refractory material is classified as

RUL	Refractory material
1350 °C	High heat duty brick
1300 °C	Intermediate heat duty brick
1100 °C	Moderate heat duty brick

Dimensional stability – Thermal expansion and contraction It is the ability of a refractory to resist any permanent change in volume when it is exposed to high temperatures for a prolonged period of time.

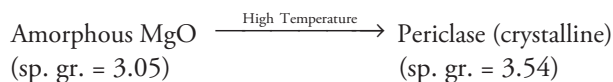
There are two types of dimensional changes.

Permanent expansion Permanent expansion occurs when one crystalline form of refractory is transformed into another crystalline form of low density. Silica brick is an example of this type. It undergoes permanent expansion. The crystalline transformation of silica brick is given below.



Permanent contraction When a refractory is subjected to high temperature for a long duration, permanent contraction occurs due to following reasons.

- Melting of low fusible constituents forming liquid which fills the pores of the refractory body causing shrinkage and vitrification, for example, fireclay bricks.
- Transformation of one crystalline form into another more dense form, for example, magnesite brick.



Thus, there is shrinkage in magnesite brick due to increase in density.

Porosity Porosity of a refractory material is the ratio of pore volume to bulk volume. All refractories contain pores. However, refractory materials with high porosity are not preferred for furnace lining because

- Molten charge, gases and slag penetrates through the pores and decreases the life of the refractory.
- Penetration of slag may change the physical nature of the inner side of the material and may result in development of internal stresses during heating.
- Refractory with high porosity has less strength, poor resistance to abrasion and greater tendency to be corroded by slags.

However, pores trap air and hence increase the resistance to thermal spalling because the trapped air acts as a non-heat conducting material.

A good refractory in general has low porosity.

Thermal spalling It is the breaking, cracking, peeling off or fracturing of a refractory material due to temperature changes. Spalling is due to rapid changes in temperature which causes unequal expansion and contraction leading to the development of internal stresses or strains. It can also be caused by the variation in the coefficient of expansion due to slag penetration in a refractory brick.

Thermal spalling can be minimised by

- Using bricks with low thermal coefficient of expansion; good thermal conductivity and of relatively high porosity within permissible limits.
- By avoiding sudden temperature changes.
- By modifying the furnace design so that stress is not set up when the furnace is heated.

Permeability It is a measure of the rate of diffusion of molten solids, liquids and gases through the interconnected pores of a refractory. Permeability increases with the rise in temperature since viscosity of the molten metal decreases.

Chemical inertness The refractory material should not react with the reactants, slag, furnace gases, fuel, ashes and products used inside the furnace. Hence, if the furnace processes acidic material, then a basic refractory should not be employed and vice versa.

Thermal conductivity In industrial operations, refractories of both low and high thermal conductivities are required, depending upon the type of furnace. Generally, furnaces are lined with refractories of low thermal conductivity to reduce heat losses by radiation, otherwise it would be difficult to maintain high temperature inside the furnace. However, in some cases, refractories of high thermal conductivity are required, for example, coke oven walls, muffle furnace and retorts which are heated from outside.

Resistance to abrasion and erosion For a refractory to last long, it should be least abraded by the descending charge, flue gases escaping at high speeds, particles of carbon, grit, etc.

Abrasion of a refractory material leads to erosion. Slags, molten gases, molten metals, etc, can also cause the corrosion and erosion of refractory lining due to the chemical reaction between the slag and the refractory lining.

Thus, a refractory material should have erosion and corrosion resistance.

Electrical conductivity Generally, all refractories, except graphite, are poor conductors of electricity. The refractories used for the lining of an electric furnace should have low thermal conductivity. While selecting a refractory, it should also be remembered that electrical conductivities of these materials increases with the rise in temperature.

Heat capacity Heat capacity of a furnace depends upon

- Thermal conductivity
- Specific heat
- Specific gravity of the refractory

Light weight refractory bricks have low heat capacity (heat capacity = $ms\Delta t$) and are suitable for intermittently operated furnaces because the working temperature of the furnace can be achieved in lesser time and with lesser consumption of fuel. Conversely, dense and heavy fireclay refractories have high heat capacity and are best suited for regenerative checker work systems used in coke ovens, stoves for blast furnaces, glass furnaces, etc.

Conditions leading to the failure of a refractory material

A refractory material can collapse if

- Refractoriness is less than the working temperature of the furnace.
- Thermal expansion is high.
- There are rapid changes in the temperature of the furnace.

- The refractory brick is heavy weight.
- The refractory brick is not properly fired.
- The brick undergoes considerable change in volume at high temperature.
- If the refractory is acidic when basic reactants/products are being processed and basic when acidic materials are being treated.

Manufacture of refractories

Manufacture of a refractory consists of the following steps

1. **Crushing** Raw materials which are generally in the form of big lumps are crushed into small uniform size particles of about 25 mm.
2. **Grinding** Crushed raw material is ground to 200 mesh size.
3. **Screening** The refractory materials are purified by screening. Unwanted materials and impurities are removed by settling, magnetic separation, froth flotation, etc.
4. **Blending and mixing** The raw materials are then mixed/blended with organic or inorganic binders like molasses, starch, shellac, gum (organic) and sodium silicate, lime, calcined gypsum (inorganic). Blending makes moulding easier by producing a homogenous mixture of the batch ingredients.
5. **Moulding** It is done either manually or mechanically by the application of high pressure. Mechanical moulding is superior to hand moulding because it produces refractories of high density and high strength whereas hand moulding produces refractories of low density and low strength.
6. **Drying** Drying removes moisture from the refractories. It is generally carried out very slowly under a selected set of humidity and temperature conditions depending upon the type of refractory.
7. **Firing or burning** This is the last step of the manufacture of refractory. Refractories are fired to stabilise and strengthen them. The reactions involved in firing are
 - Dehydration
 - Calcination
 - Oxidation
 - Shrinkage
 - Crystal structure transformation (vitrification)

The bricks are generally fired at a temperature higher than the temperature at which they are used. Firing is done in tunnel kilns or shaft kilns or rotary kilns. The firing temperatures of different bricks are: 1480 °C for high fired super duty bricks; 1700 °C for kaolin bricks and 1870 °C for some basic bricks.

The whole manufacturing process can be summarised in the flow chart given in Figure 5.11.

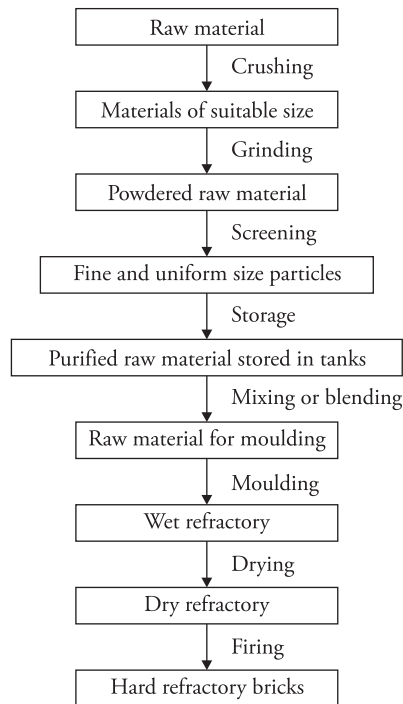


Figure 5.11 Flow chart of manufacture of refractory

Silica bricks (acidic refractories)

They contain 90%–95% SiO_2 to which about 2% lime is added to improve its binding properties. Raw materials used are quartz, quartzite, sand, sandstone, etc. The raw materials are crushed and ground with 2% lime and water. The thick paste is moulded by hand or machines. The bricks are then dried in air or in heated rooms and then burnt in kilns.

Firing is the most important step in the manufacture of silica bricks and is usually done in a continuous tunnel under a temperature range of 1400 °C–1800 °C for nearly 12 hours, so that quartzite is converted into cristobalite. After this, slow cooling is done for one to two weeks so that cristobalite changes to tridymite. Thus the final refractory brick is a mixture of tridymite and cristobalite.

Quartzite (Crystalline)	↔	tridymite (α form of silica)	↔	cristobalite (β form of silica)
sp. gr = 2.65		sp. gr = 2.26		sp. gr = 2.32

The manufacturing process can be summarised in the flow chart given in Figure 5.12.

If during firing of silica bricks, quartzite is not converted into tridymite and cristobalite, the bricks will expand to about 17.2% during use in the furnace and the refractory structure will fall.

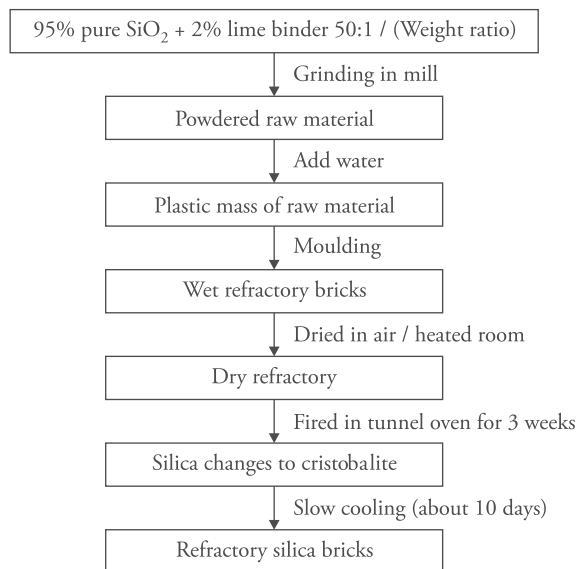


Figure 5.12 Flow chart of the manufacture of silica bricks

Properties

- They are yellow in colour with brown specks distributed throughout. Colour varies with the raw material used.
- Approximate composition

Content	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO
Weight %	96–97	2	0.75	0.5	0.5

- They are acidic in nature and are suitable for furnaces treating acidic charges/slugs.
- Their porosity is low (17%–25%).
- They can withstand a load of about 3.5 kg/cm² up to 1500 °C–1600 °C.
- Their fusion temperature is about 1750 °C.
- They are light and possess high rigidity and mechanical strength.
- These bricks do not contract in use.
- Silica bricks are not susceptible to thermal spalling at temperature below 800 °C.

Applications

- Lining of roof arches of open hearth furnaces and reverberatory furnaces, gas retorts and walls of coke ovens.
- Silica bricks are widely used in iron and steel industries.

Fireclay refractory

Fireclay bricks are made from finely ground soft plastic material. Fireclay also called kaolinite or hydrated aluminium silicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is mixed with calcined fireclay called 'grog' (fireclay already heated to 1300°C). Grog generally accounts for 50% or more of the raw material (batch). The exact proportion of the constituents depends upon the type of bricks to be made. Greater the percentage of grog, lesser will be the thermal spalling. Generally, the composition ranges from 55% SiO_2 and 35% Al_2O_3 (feebly acidic) to 55% Al_2O_3 and 40% SiO_2 (nearly neutral bricks), the remaining being K_2O , FeO , CaO , MgO , etc. Figure 5.13 gives the flow chart for the manufacture of fireclay bricks.

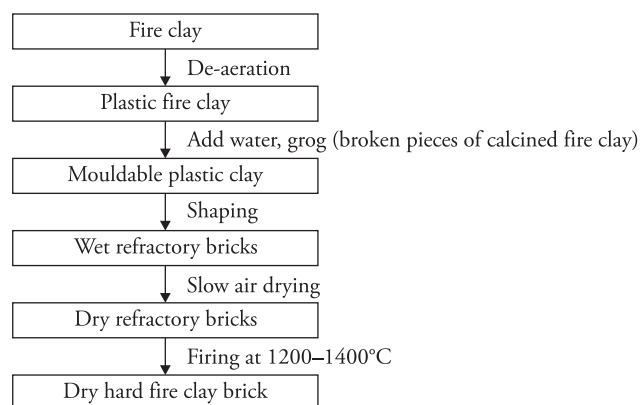


Figure 5.13 Flow chart of the manufacture of fireclay bricks

Properties

- They are light yellow to reddish brown depending on the content of iron oxides.
- They are slightly acidic in nature.
- They are strong. Properly fired bricks are as hard as steel.
- Approximate composition:

Content	Silica	Alumina	Lime	Iron	Alkali	Magnesia
Weight (%)	45–63	30–45	0.1–0.6	1–2.5	1.0	0.5

- They have low porosity (8% to 24%), higher resistance to thermal spalling compared to silica bricks. As mentioned before, greater the percentage of 'grog', greater is the resistance to thermal spalling.
- Their safe working temperature is about 1545°C . They have a softening temperature of 1350°C under a load of 2 kg/cm^2 .
- They have high crushing strength (about 200 kg/cm^2) which goes down with increasing temperature.

Applications

- Used in steel industries for the lining of blast furnaces, open hearths, stoves, ovens, crucible furnaces, etc.
- Since these bricks have better resistance to thermal spalling than silica bricks, they are used for making checker works of regenerative furnaces.
- Fireclay refractories are also widely used in foundries, lime kilns, regenerators, pottery kilns, glass furnaces, brass and copper furnaces, etc.

5.7 Abrasives

Introduction

The word ‘abrasive’ comes from *abrade* which means ‘to wear off by rubbing’. An abrasive is a hard material, often a mineral, which is used to machine, grind or finish a work piece through extensive rubbing. Rubbing removes sharp edges and the unwanted roughness of the surface and makes it smooth. Commonly used abrasives are pumice stone, sandstone, emery, etc.

Properties of abrasives

The three important properties of abrasives are as follows:

- Hardness
- Fracture resistance
- Wear resistance

Hardness It is the ability of the abrasive to cut the surface of the material that is being polished. It is a very important property and is measured roughly on Moh’s or Vicker’s scale.

Fracture resistance It is the toughness of the abrasive that is the tendency of an abrasive material to resist breaking and crumbling during grinding and polishing.

Wear resistance It is the ability of the abrasive to resist wear and remain sharp. Wear resistance of an abrasive is directly proportional to its hardness.

Classification of abrasives

Abrasives may be classified as natural or artificial. Natural abrasives are minerals that occur in nature and artificial abrasives are synthetic or man-made abrasives. Except diamond (a natural abrasive), artificial abrasives are generally harder than natural abrasives.

A. Natural abrasives Some common naturally occurring abrasives are as follows.

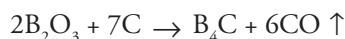
- Diamond** It is crystallised carbon. It is the hardest material known and is the only significant natural abrasive. Industrial diamonds are known as black or bort diamonds (diamonds that are off-colour or faulty are known as borts). They are less expensive than clear diamonds used for jewellery. Diamonds (borts) are used in drill points as saw teeth for cutting rocks, stone or grinding wheels. Diamond grinding wheels are used to grind

very hard material like carbide cutting tools, glass, ceramics and stone. Fine diamond dust is used to make polishing compounds for finishing hardened steel and other very hard materials.

- (ii) *Corundum* It is crystallised aluminium oxide (Al_2O_3) and comes next to diamond in hardness. Gemstones such as emeralds and ruby are the purest form of corundum. Impure corundum finds use as an abrasive for grinding glasses, gems, lenses, metals and in metal cutting.
- (iii) *Emery* It is a combination of corundum and iron oxide and is one of the oldest natural abrasives used for metal working. It contains 55%–75% crystalline alumina, 20%–40% magnetite (Fe_3O_4) and about 12% other materials. Emery is not as sharp as artificial abrasives and its grinding power depends upon the quantity of alumina present. It is used largely for hand polishing.
- (iv) *Garnets* They are trisilicates of alumina, magnesia and ferrous oxide. Garnets are quite soft and hence cannot be used for grinding steel and iron, but when glued to paper or cloth they are used for finishing hardwoods.
- (v) *Other common natural abrasives* are walnut shells used for cleaning aircraft engine parts, sand used for sharpening wood working tools, quartz used as sandpaper for wood and for fine grinding of glass. Quartz particles cemented together with feldspar, clays and other minerals are used for grinding floor, ores, etc.

B. Artificial abrasives

- (i) *Carborundum or silicon carbide (SiC)* It is manufactured by subjecting a mixture of sand, coke and saw dust to high temperature (1650 °C–2200 °C) in an electric furnace. A bluish mineral with hardness between corundum and diamond crystallises out. It is very hard, chemically inert and can withstand high temperatures. It finds use as refractory material, as a heating element in electrically heated industrial furnaces, for making grinding wheels. On an abrasive paper or cloth it is used for finishing wood works. It is generally used for polishing or grinding materials of low tensile strength like cast iron, aluminium, bronze, copper, rubber, marble, glass, ceramics pottery, plastics and fibre.
- (ii) *Aluminium oxide (Al_2O_3)* It is prepared by subjecting a mixture of calcined bauxite, coke and iron in an electric furnace at very high temperature (about 4000 °C). It is not as hard as silicon carbide but is tougher and does not fracture easily. It finds use in the grinding and polishing of materials of high tensile strength like carbon steels, alloy steels, hard steels, wrought iron, etc. It is sold under a number of trade names such as alundum, aloxite, borolon, exolon, etc.
- (iii) *Boron carbide* It is inert and one of the hardest of all artificial abrasives. Boron carbide is made by heating boron oxide with coke in an electric furnace to approximately 2700 °C.



It is harder than both aluminium oxide and silicon carbide but is not as hard as diamond. It is used for making grinding dies and for cutting and sharpening very hard materials. It is sold under the trade name Norbide.

Both natural and synthetic abrasives are available in a variety of shapes. The commonly used shapes are as follows:

- (i) *Bonded abrasives* Bonded abrasives are composed of a binder and an abrasive. The binder used is often clay, a resin, glass or rubber. The mixture of binder and abrasive is then shaped into blocks, sticks or wheels.
- (ii) *Coated abrasives* Coated abrasives are those in which the abrasive is bonded to a backing material with an adhesive. The backing material can be paper, cloth, rubber, resin, polyester or even metal. It is generally flexible and available in the form of belts, rolls, sheets, etc. Sand paper is a very commonly used coated abrasive.
- (iii) *Non-woven nylon abrasives* They are three-dimensional open weave nylon materials coated with abrasives. They come as pads, wheels and brushes.
- (iv) *Metal bonded abrasives* Abrasives like diamond are held together in a metal matrix to form metal bonded abrasives.

Abrasives find use in every walk of life. A house wife uses abrasives to keep utensils clean, scrubbers are used for cleaning tiles, to sharpen knives, dentists use abrasive powder for cleaning the teeth, Abrasives like almonds, oat meal are used to exfoliate dead skins. Besides this, abrasives are used in industry for grinding, polishing, buffing, honing, cutting, drilling and sharpening.

5.8 Insulating Materials

Introduction

Insulating materials are those substances which resist the flow of heat, sound and electricity through them. There are three types of insulators.

1. *Thermal insulators* They resist the flow of heat. Examples include cork, fibre boards, asbestos, glass wool and foamed polystyrene slabs.
2. *Electrical insulators* Also called dielectrics, these materials resist the flow of electric current. Perfect insulators do not exist, but some materials such as glass, paper and teflon which have high resistivity are regarded as good electrical insulators.
3. *Sound insulators* They check the flow of noise from the source to the surroundings. Examples include fibre boards, acoustic plaster and boards and cellular concrete.

We shall discuss thermal and electrical insulators in the forthcoming sections.

Thermal insulation

Thermal insulation is the reduction of heat transfer between objects in thermal contact or in the range of a radiative influence. A substance that reduces this rate of heat flow is a thermal insulator. A thermal insulating material is placed between a warm region and a cooler region to reduce the rate of heat flow to the cooler region.

Properties of thermal insulators A thermal insulator should have

- (i) *Thermal stability*, that is, it should be able to withstand the working temperature without deteriorating.
- (ii) *Dimensional stability* Its dimensions should not change at the operating temperature.
- (iii) *Chemical stability* It should be chemically inert and not affect other materials.

- (iv) *Air permeability* It is the ability of a material to allow air to flow through its pores. Good insulators have high air permeability since air is a poor conductor of heat.
- (v) It should have low thermal conductivity and low specific heat.
- (vi) It should be resistant to vibration and shock.
- (vii) It should be odourless.
- (viii) It should be non-inflammable (fire proof).
- (ix) It should be light in weight.
- (x) It should be vermin proof.
- (xi) It should be cost-effective and economical.
- (xii) It should be water proof.

Factors affecting insulation resistance

- (i) *Moisture* It adversely affects thermal insulation because thermal conductivity of water is almost 25 times that of air.
- (ii) *Temperature* Insulation resistance is inversely proportional to temperature.
- (iii) *Age/time* Thermal insulation decreases with the passage of time because of the aging of the insulating material.

Thermal insulating materials Thermal insulators can be

- (i) *Organic material* Examples include wool, wood, pulp, cork, sawdust, sugarcane fibre, cardboard, paper and leather.
- (ii) *Inorganic materials* Examples include air, glass wool, charcoal, slag, coke, powder and asbestos.

Applications

- (i) *Buildings* Thermal insulation of building makes them energy efficient and provides more uniform temperatures throughout the space. It makes the building comfortable by keeping it warm during winter and cool in the summer season. Unlike heating and cooling equipment, thermal insulation is permanent and does not require any maintenance.
- (ii) *Industries* In cold storage plants, insulators like cork and rock wool impregnated with waterproof binder are used for insulating cold surfaces. Asbestos is used for cooling surfaces at temperature up to 149 °C. A mixture of 85% magnesium carbonate and 15% asbestos fibre commonly known as 85% magnesia is used to maintain temperature up to 315 °C. In industries, thermal insulators help to maintain high and low temperatures as per requirement.
- (iii) *Clothing* To withstand low ambient temperatures, a thick insulation is desirable to reduce the convective heat loss. Examples include wool, which acts as a thermal insulator and helps to maintain body temperature during the cold season.

Similarly, cotton fabrics help to offset the high surrounding temperatures during the summer season. Cotton clothing enables the sweat to evaporate thus permitting cooling by evaporation.

- (iv) *Spacecraft* During entering and leaving the atmosphere, spacecraft faces high temperature due to compression of air at high speeds. Insulators like carbon composite materials and silica fibre tiles help to maintain the temperature of the aircraft when it enters or leaves the atmosphere.

Electrical insulators

They are poor conductors of electricity. The principal function of an insulating material is to allow current to flow through a conductor without permitting it to leak off. This is achieved by isolating or separating the electrical conductor from the nearby electrical path. Electrical insulation is used wherever electricity is put to work. It is used in electric equipments ranging from giant generators, transformers and distribution lines to microscopic integrated circuits. Air, glass, oil and polyethene are some common examples of electrical insulators.

Properties of electrical insulators

- (i) *High resistivity* Electrical resistance is the ability to impede electric current from passing through. Even the best electrical insulating materials allow some current to pass when voltage is applied. This current is due to the ions in the insulator, which move under the influence of the electric field. An electrical insulator should, however, have very high electrical resistance.
- (ii) *Breakdown voltage* It is also called dielectric strength. At extremely high voltage, all insulators conduct heat and electricity and lose their insulating abilities. The voltage at which this change occurs is known as the dielectric strength or the breakdown voltage. A good electrical insulator is one which has high dielectric strength or breakdown voltage.
- (iii) *Atomic structure* The valence electrons in insulators must be tightly held together. This prevents them from moving.
- (iv) *Air permeability* The higher the air permeability, greater is the electrical resistance as air is a poor conductor of electricity.
- (v) *Chemical properties* Electrical insulators must be chemically inert, have resistance to flammability, resistance to reaction with water, should not react with oxygen as oxygen and moisture degrade the insulating property.
- (vi) *Mechanical properties* Electrical insulators should have high mechanical strength, flexibility, high tear and tensile strength, shear strength and abrasion resistance.

Important electrical insulators and their applications

Gases, liquids and solids are used as electrical insulating materials.

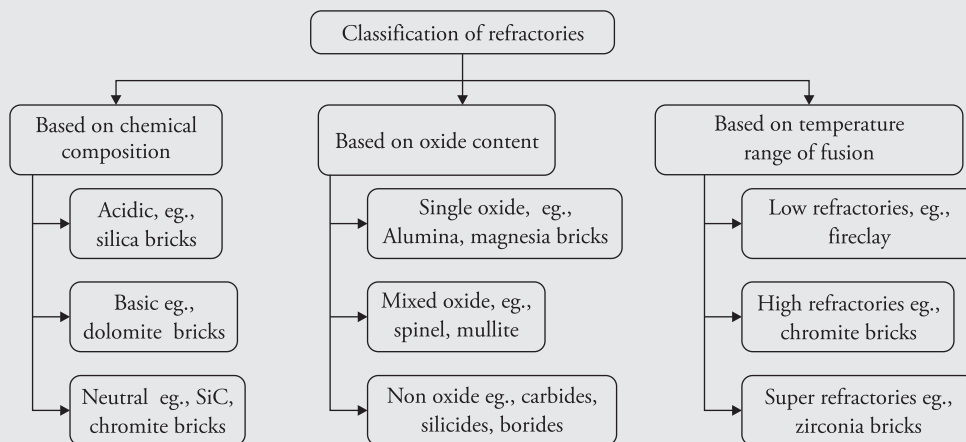
- (i) **Gases** Air is used as an insulator to insulate high voltage transmission lines. High-voltage transformers use sulphur hexafluoride because of its high dielectric strength.
- (ii) **Liquids** Insulating liquids like oils and chlorinated hydrocarbons are used in cables, capacitors, transformers and circuit breakers. Liquids have higher electric strengths and better heat dissipation properties than gases.
- (iii) **Solids**
 - *Ceramics and porcelain* (aluminium silicate) This is a widely used insulator. However, porcelain should be free from porosity and should be glazed so that water is not traced on it.
 - *Glass* is popularly used in transmission and distribution systems. It has high dielectric strength, high resistivity, low coefficient of thermal expansion, high tensile strength compared to porcelain. However, moisture and dust collect on glass surfaces providing an alternative path to the leakage current of the system.

- *Polymers* Polyethylene, polypropylene and polystyrene are examples of thermoplastics used in electrical insulation. Phenolics, epoxies and silicones are thermosetting plastics used in electrical insulation.
- *Mica* Sheet mica is used primarily in electrical equipments and appliances in the form of washers, spacers, sleeves, tubes, etc., where high voltage must be withstood.
- *Laminates* Made of woven cloths, papers and mats impregnated with thermosetting resin such as phenolic, epoxy or melamine resins are used in printed circuits.

Summary

- Cement is a binder, a substance that sets and hardens independently and can bind other materials together. It is used in the construction industry for binding materials like bricks, building stones, tiles and is also used for flooring and plastering purposes.
- Chemically cement is a mixture of silicates and aluminates of calcium. It consists of C_3S , C_2S , C_3A and C_4AF .
- Cement can be prepared by
 - Rotary kiln method
 - Vertical shaft kiln method
- The various steps in the manufacture of cement are:
 - Mixing (dry or wet mixing)
 - Burning
 - Cooling
 - Grinding
 - Packing and supply
- When cement is mixed with water and allowed to stand, it changes to a hard rigid mass. This is known as setting. Gradually, the rigid mass gains strength to form a compact rock like material. This development of strength due to crystallisation is called hardening.
- Setting and hardening of cement takes place due to hydration and hydrolysis reactions of the various constituents of cement.
- C_3A causes initial setting of cement. Gypsum is added to reduce the initial setting rate of cement.
- Glass is a supercooled liquid consisting of a mixture of silicates.
- General representation of glass is $x R_2O.y MO.6SiO_2$.
- Glass is manufactured in a tank furnace or pot furnace.
- Raw materials for the manufacture generally include limestone, Na_2CO_3 and SiO_2 .

- The manufacturing process can be divided into four steps:
 - (i) Melting
 - (ii) Forming and shaping
 - (iii) Annealing
 - (iv) Finishing
- **Annealing** is the process of slow cooling of glass which is used to reduce the strain.
- **Devitrification** is the process of crystallisation of glass and is considered as a deformity in glass.
- There are wide varieties of glasses depending on their constitution.
- Some common varieties of glasses are soda glass or soft glass, potash glass or hard glass, lead glass or flint glass, borosilicate glass or pyrex glass or jena glass, aluminosilicate glass, optical or Crook's glass or phosphate glass, safety glass or laminated glass, toughened glass, wired glass, glass wool, 99.5% silica glass or vitreosil, polycrystalline glass, neutral glass, photo chromatic glass, insulating glass.
- A refractory is a substance which can withstand high temperature without softening or deformation in shape.
- A good refractory should be chemically inert, have high fusion temperature and less pores, should not break under temperature fluctuations and should be resistant to corrosion, abrasion and erosion.



- Refractoriness is the ability of a refractory to withstand high temperature without appreciable deformation or softening. It is determined by seger cone test.
- Refractoriness under load (RUL) is the fusion temperature of a refractory under a load of 3.5–1.75 kg/cm².
- Dimensional stability is the tendency to resist permanent expansion or contraction.

- Silica bricks undergo permanent expansion on heating. Magnesite bricks undergo permanent contraction on heating.
- Thermal spalling is the breaking, or peeling off of a refractory material due to temperature changes.
- Porosity is the ratio of pore volume to bulk volume. Refractories of low porosity are generally preferred.
- Various steps in the manufacture of refractories are crushing, grinding, screening, blending and mixing, moulding, drying, firing or burning.
- Abrasives are materials that are used to smoothen a rough surface by extensive rubbing.
- The important properties of abrasives are hardness, fracture resistance and wear resistance.
- Abrasives can be classified as natural and artificial.
- Diamond, corundum, emery, garnets and walnut shells are some commonly used natural abrasives which find use in grinding, polishing and cutting of hard surfaces.
- Silicon carbide, aluminium oxide and boron carbide are common synthetic abrasives.
- Both natural and synthetic abrasives can be bonded or coated.
- Insulating materials are those substances which resist the flow of heat, sound or electricity through them.
- Thermal insulators resist the flow of heat and find use in the insulation of buildings and in industries to maintain both high and low temperatures.
- Electrical insulators resist the flow of electric current.
- Gases like sulphur hexafluoride, liquids like oils and chlorinated hydrocarbons, solids like ceramics, porcelain, glass, polymers, mica, etc. are the commonly used electrical insulators.
- Electrical insulators are used to insulate conducting materials and allow their safe handling.

Review Questions

1. Describe the 'wet process' of manufacture of cement by the rotary kiln method.
2. What do you mean by setting and hardening of cement? Discuss the various reactions involved with the help of equations. What is the role of gypsum in cement?
3. What are the constituents of cement? Explain the role of each constituent.
4. Draw a flow chart of the manufacture of Portland cement by rotary kiln method. Also write the chemical reactions involved in the process.
5. Explain the manufacture of cement by vertical shaft kiln method.

6. What are the ISI specifications of Portland cement?
7. Define cement. Classify the different types of cements.
8. What are the different methods of manufacturing cement. Explain their relative merits and demerits.
9. 'The properties of Portland cement depend on the relative proportions of its constitutional compounds.' Comment on the statement.
10. Write short notes on the following:
 - (i) Setting and hardening of cement.
 - (ii) Soundness of cement.
 - (iii) Mortar and concrete.
 - (iv) Physical requirements of cement.
 - (v) Raw materials for the manufacture of cement.
 - (vi) Chemical composition of cement.
 - (vii) Types of cements
11. What is glass? Describe the manufacture of glass with the help of a well labelled diagram.
12. What is glassy state of matter? Why is annealing important in the manufacture of glass?
13. What is devitrification of glass? Discuss the causes of devitrification. How can it be avoided and what are its disadvantages?
14. Give the classification of glass. Write down the uses of various types of glasses.
15. Write short notes on
 - (i) Importance of annealing
 - (ii) Devitrification of glass
 - (iii) Borosilicate glass
 - (iv) Glass wool
 - (v) Laminated glass
 - (vi) Optical glass
 - (vii) Toughened glass
 - (viii) Photochromatic glass
16. What are refractory materials? How are they classified? What are the qualities of a good refractory?
17. The refractory for a furnace lining has to be chosen on the basis of its nature and nature of chemicals used in the furnace. Justify the statement with suitable examples.
18. What is refractoriness of a refractory material? Explain the seger cone test for the determination of refractoriness.
19. Write short notes on:
 - (i) RUL test of refractory materials.
 - (ii) Dimensional stability.

- (iii) Porosity.
 - (iv) Thermal spalling.
20. What are acidic refractories? Explain the preparation, properties and uses of silica bricks.
 21. How are fireclay refractories manufactured? Explain their properties and uses.
 22. What are abrasives? Discuss the important properties of abrasives.
 23. Explain in detail the classification and uses of abrasives.
 24. What are insulating materials? Classify them and discuss the properties of electrical and thermal insulating materials.
 25. What are thermal insulators? Discuss the applications of thermal insulators.
 26. What are electrical insulators? Name the common electrical insulating materials and write down their applications.

Multiple Choice Questions

1. The raw materials used for the manufacture of cement are
 - (a) Calcium carbonate
 - (b) Sandstone
 - (c) Gypsum
 - (d) All of the above
2. The cement used for foundation works in areas containing water and salts (sea water) is
 - (a) Ordinary Portland cement
 - (b) Coloured cement
 - (c) Super sulphate cement
 - (d) Rapid hardening cement
3. Which of the following is not contained in the clinkers
 - (a) C_2S
 - (b) C_4AF
 - (c) C_3A
 - (d) C_3F
4. The role of gypsum in cement is
 - (a) To impart proper colour to cement
 - (b) To increase the rate of hardening of cement
 - (c) To delay the setting rate of cement
 - (d) To increase the setting rate of cement
5. When water is added to cement it hydrates, which of the following compounds is responsible for the immediate stiffening of cement (flash set)
 - (a) C_3A
 - (b) C_2S
 - (c) C_3S
 - (d) C_4AF
6. Setting and hardening of cement is completed in – days
 - (a) 2–5 days
 - (b) 15–30 days
 - (c) 10–15 days
 - (d) 25–45 days

7. Plaster of Paris is
 - (a) $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$
 - (b) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
 - (c) Both a and b
 - (d) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
8. Glass is
 - (a) An amorphous solid
 - (b) A crystalline solid
 - (c) Can be either amorphous or crystalline
 - (d) Neither amorphous nor crystalline
9. The furnace used for the preparation of glass is
 - (a) Rotary kiln
 - (b) Blast furnace
 - (c) Tank furnace
 - (d) Reverberatory furnace
10. The glass used in microwave ovens, in laboratory for making high quality glass wares, boiling tubes, flasks etc.
 - (a) Borosilicate glass
 - (b) Soda glass
 - (c) Potash glass
 - (d) Optical glass
11. Which of the following is used in bullet proof glass
 - (a) Toughened glass
 - (b) Laminated glass
 - (c) Flint glass
 - (d) Wired glass
12. The breaking, cracking, peeling off or fracturing of a refractory material due to temperature changes is
 - (a) Thermal fracturing
 - (b) Thermal spalling
 - (c) Thermal cracking
 - (d) Dimensional stability
13. The refractoriness of a refractory is measured by the
 - (a) Seger cone test
 - (b) RUL test
 - (c) Viscosity index test
 - (d) Compression factor
14. Which of the following refractory undergoes permanent contraction on heating
 - (a) Silica bricks
 - (b) Graphite bricks
 - (c) Magnesite bricks
 - (d) Dolomite bricks
15. Which of the following is not a basic refractory
 - (a) Magnesite bricks
 - (b) Dolomite bricks
 - (c) Chrome-magnesite refractories
 - (d) Zirconia refractories
16. A hard material used to machine, grind or finish a work piece through extensive rubbing
 - (a) Abrasive
 - (b) Cutter
 - (c) Refractory
 - (d) None of the above

17. Which of the following is not a natural abrasive
(a) Diamond (b) Corundum
(c) Carborundum (d) Garnets
18. Insulating materials resist the flow of
(a) Heat (b) Electricity
(c) Sound (d) All

Solutions

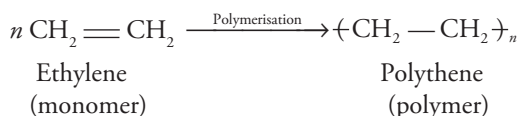
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| 9 (c) | 10 (a) | 11 (b) | 12 (b) | 13 (a) | 14 (c) | 15 (d) | 16 (a) |
| 17 (c) | 18 (d) | | | | | | |

Chapter 6

POLYMERS

6.1 Introduction

Polymers are compounds of very high molecular weights formed by the combination of a large number of small repeating units. The word 'polymer' is derived from the Greek word *poly* meaning 'many' and *mer* meaning 'part'. The process by which the simple molecules (monomers) are converted into polymers is called polymerisation. For example, many ethylene molecules combine to form a giant molecule of polythene.



where n = number of monomers in the polymeric chain.

The number of repeating units in a polymeric chain is called 'degree of polymerisation'. In the above example, ' n ' is the degree of polymerisation.

Polymers are also called *macromolecules* because of their big size. In fact, the terms polymers and macromolecules are often used synonymously. However, strictly speaking, a polymer contains repeating units (monomers), whereas a macromolecule is a giant molecule that may or may not contain monomer units. For example, chlorophyll and haemoglobin are macromolecules but not polymers.

Polythene may be regarded as a polymer as well as a macromolecule because it contains a large number of repeating units. Thus, all polymers are macromolecules and not *vice versa*.

6.2 Classification of Polymers

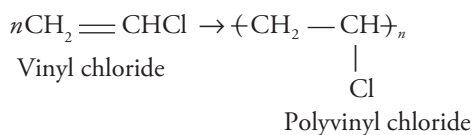
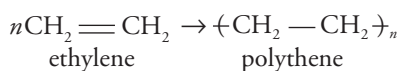
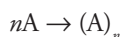
Polymers may be classified in various manners.

1. **On the basis of origin** On the basis of origin, polymers are of two types:
 - (a) Natural polymers
 - (b) Synthetic polymers

- (a) **Natural polymers** They are polymers that occur in nature. For example, starch (polymer of α -D-glucose), cellulose (a polymer of β -D-glucose), proteins (polymer of α -amino acids) and natural rubber (a polymer of poly-cis-isoprene).
- (b) **Synthetic polymer** It is a polymer that is prepared artificially in the laboratory. For example, polyethylene (PE), polyvinylchloride (PVC), nylon, terylene, bakelite, synthetic rubber, etc.

2. On the basis of monomer composition

- (a) **Homopolymer** If a polymer consists of identical monomers, it is termed as homopolymer.



- (b) **Copolymer** If a polymer is made up of more than one type of monomers it is called a copolymer.



Depending on the arrangement of the monomeric units, the copolymers may be further classified as

- (i) **Random copolymers** The monomeric units are randomly arranged.



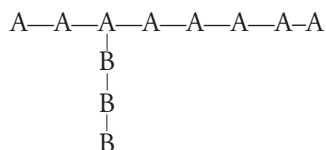
- (ii) **Alternating copolymers** The monomeric units are arranged in an alternating manner.



- (iii) **Block copolymers** The monomeric units are arranged in blocks.



- (iv) **Graft copolymers** They are branched copolymers in which the backbone is formed of one type of monomer and the branches are formed of the other types of monomers.



3. **On the basis of chain structure**

- (i) **Linear polymer** It has no branching other than the pendant groups associated with the monomer. Linear polymers are well packed and therefore have high densities. For example, polythene, nylons and polyesters.
- (ii) **Branched polymers** These are polymers in which the monomers are joined to form long chains with side chains or branches of different lengths. They are irregularly packed and have low densities. If the side chain is different from parent chain, they are called graft polymers. For example, low-density polyethene, glycogen, etc.
- (iii) **Cross-linked polymers** These are polymers in which the monomer units are linked together to form a three-dimensional network. These polymers are hard, rigid and brittle. They are also called network polymers. For example, bakelite, vulcanised rubber, etc.

4. **Based on chain composition**

- (i) **Homochain polymer** Polymers having all carbon atoms along their backbone are called homochain polymers. For example, polyethene, PVC, rubber, etc.
- (ii) **Heterochain polymer** If the polymeric chain contains a heteroatom, then they are called heterochain polymers. For example, nylon (polymeric chain contains nitrogen atom) and terylene (polymeric chain contains oxygen atom).

5. **Based on polymerisation mechanism**

- (i) **Addition polymers** Those polymers that are obtained by the addition of monomeric units are called addition polymers. The molecular weight of such a polymer is an exact multiple of the molecular weight of the monomer.

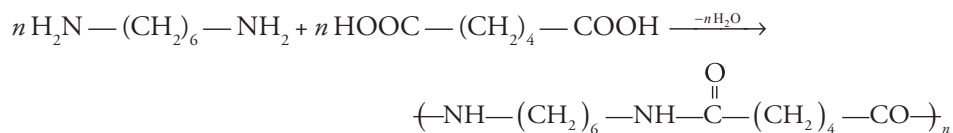


Molecular weight of polymer = $n \times$ molecular weight of monomer.

For example, polyethene, PVC, etc.

- (ii) **Condensation polymers** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia and hydrochloric acid is termed as a condensation polymer. The molecular weight of such a polymer is not an exact multiple of the molecular weight of the monomer.

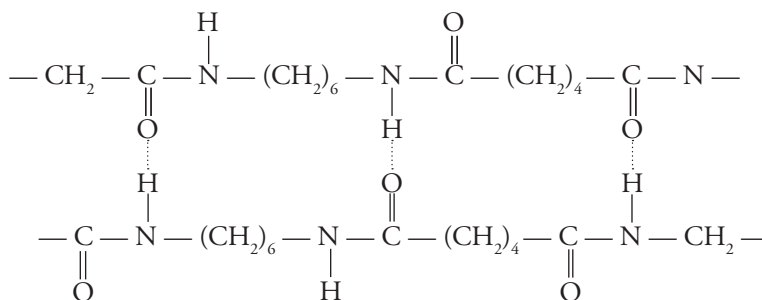
For example, Nylon 66 is obtained by the condensation of two monomers, hexamethylenediamine and adipic acid with the loss of water molecules.

6. **Based on molecular forces**

- (i) **Elastomers** They are polymers held by weakest intermolecular forces and have elastic behavior. For example, natural rubber. These can be stretched to at least thrice their

original length but return to their original shape and dimension as soon as the stretching force is removed.

- (ii) **Fibres** These are polymers whose polymeric chains are held together by strong intermolecular forces like hydrogen bonds or dipole–dipole interactions. They are crystalline in nature and have high tensile strength. For example, nylon 66, polyester, silk, etc.



Hydrogen bonding in Nylon 66

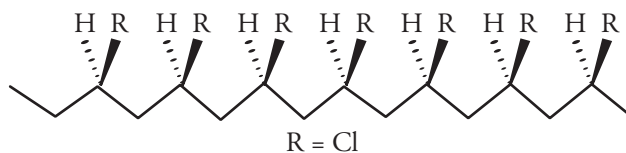
- (iii) **Thermoplastics** They are linear, long-chain polymers that soften on heating and harden when cooled. The intermolecular forces of these polymers are intermediate between those of elastomers and fibres. There is no cross-linking between the polymeric chains. They can be processed again and again.

For example, polyethene (PE), polystyrene, PVC, teflon, polypropylene, etc.

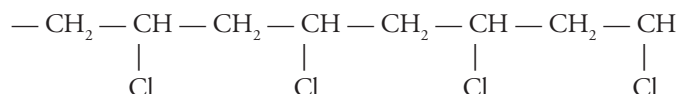
- (iv) **Thermosetting plastics** They are polymers that can change irreversibly into hard and rigid materials on heating and cannot be reshaped once they set. They form hard, infusible, insoluble products because of cross-linkages. For example, bakelite, melamine, etc.

7. **Based on tacticity** Tacticity is defined as the spatial arrangement of the substituent groups on the asymmetric carbon atom. Based on the orientation of side groups in space the polymers can be of three types

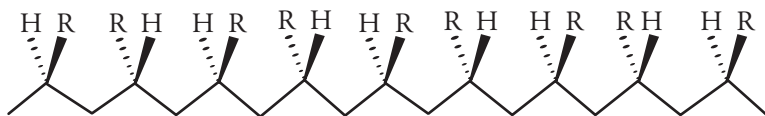
- (i) **Isotactic polymers** When the orientation of side groups (R) on all asymmetric carbon atoms is the same, the polymer is termed as an isotactic polymer



For example, PVC.



- (ii) **Syndiotactic polymer** When the orientation of the side groups on alternate asymmetric carbon atoms is the same, the polymer is termed as a syndiotactic polymer.



- (iii) **Atactic polymer** When the side groups have no preferential arrangement and are randomly arranged, the polymer is called an atactic polymer.



In general, isotactic and syndiotactic polymers are partially crystalline, whereas atactic polymers are amorphous, indicating the absence of crystalline order.

8. Based on degree of polymerisation

- (i) **Oligopolymers** Polymers with low degree of polymerisation are called 'oligopolymers'.
 (ii) **Macromolecules** Polymers with a high degree of polymerisation are called 'high polymers'. They have very high molecular weights (10^4 – 10^6) and hence are called macromolecules.

9. Based on chemical composition

- (i) **Organic polymers** A polymer whose backbone chain is made mainly of carbon atoms and the side chains consist of oxygen, nitrogen, sulphur, etc. Examples include polythene, PVC, nylon, etc.
 (ii) **Inorganic polymers** These polymers do not have a carbon backbone chain. Examples include silicone rubbers, phosphazene, etc.

The classification of polymers is summarised in Figure 6.1.

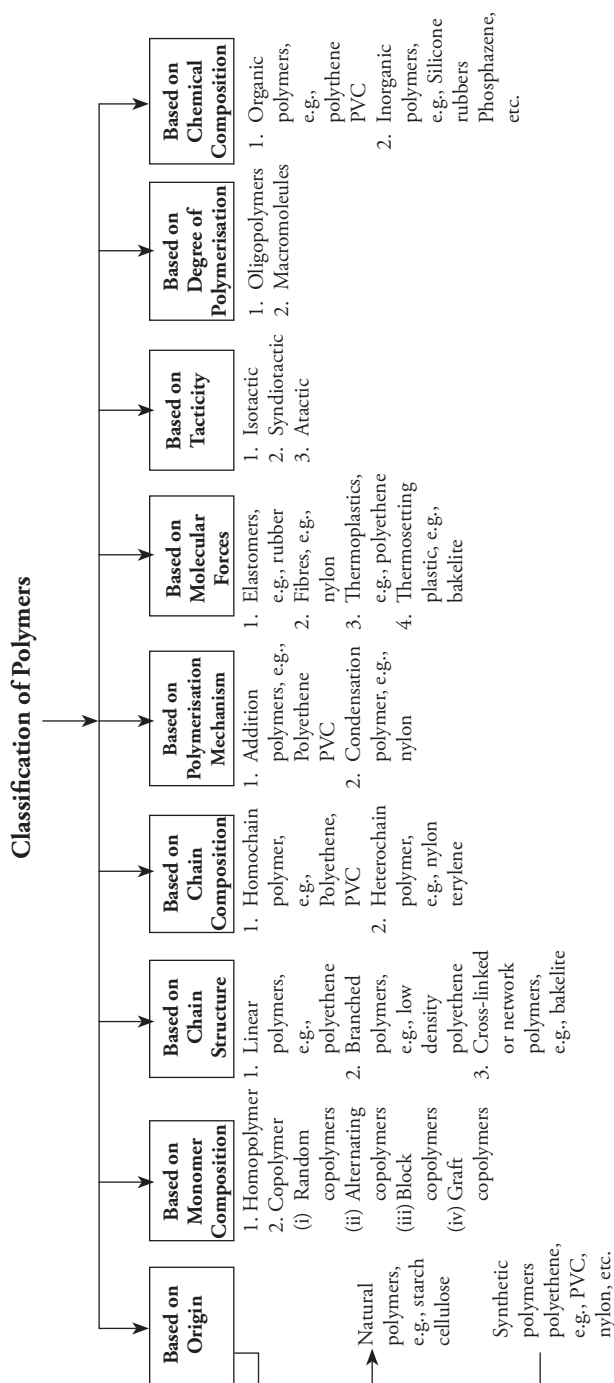


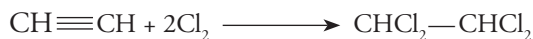
Figure 6.1 Classification of polymers

6.3 Functionality

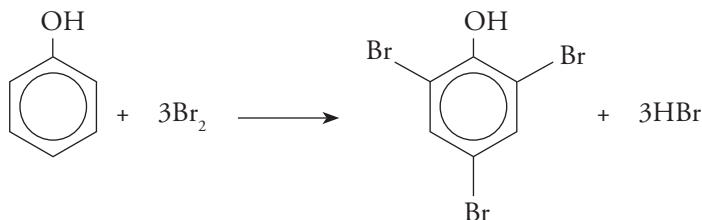
The number of reactive sites in a molecule is termed as its functionality. For a molecule to act as a monomer it must have at least two reactive sites, that is, its functionality should be two. For example, ethylene can add two molecules of hydrogen or halogen. Hence, it is bifunctional (functionality two).



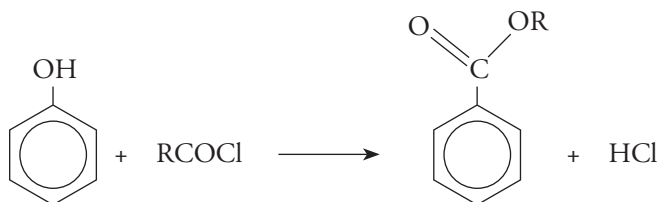
Similarly, acetylene has a functionality of four (tetrafunctional), as it can react with four atoms of hydrogen or halogen.



Similarly, phenol has three reaction sites (2-ortho and one para). It undergoes substitution reaction at these sites. Hence, it is trifunctional.

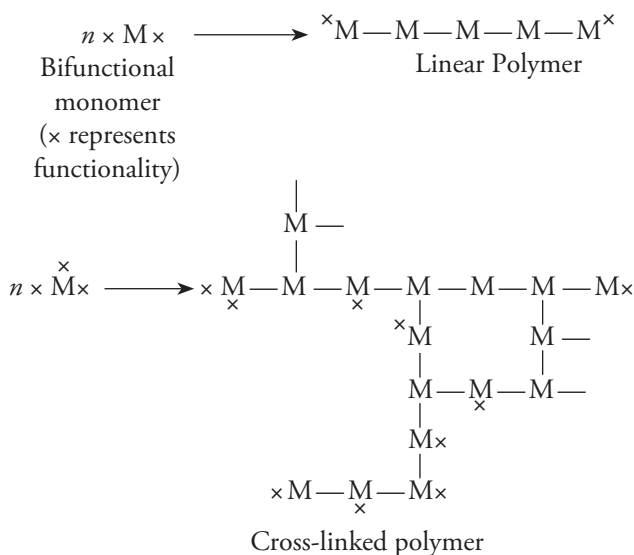


Phenol also exhibits a functionality of one as shown below.



Depending on functionality of the monomers used, we get linear, branched or three-dimensional cross-linked polymers.

If the monomer is bifunctional (ethylene, propylene, vinyl chloride, styrene, etc.), a linear polymer is formed. A trifunctional monomer leads to the formation of a cross-linked polymer, whereas a mixture of bifunctional and trifunctional monomer may form branched or cross-linked polymer.



6.4 Mechanism of Polymerisation

There are two types of polymerisation processes:

1. Addition polymerisation or chain polymerisation
2. Condensation polymerisation

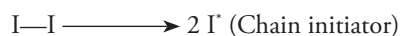
1. **Addition polymerisation or chain polymerisation** In this type of polymerisation, the monomer molecules are added to each other without the formation of any byproduct. The elemental composition of polymer is similar to that of the monomer and its molecular weight is an exact multiple of the molecular weight of the original monomeric molecule.

Bifunctional molecules like ethylene, propylene (olefins), vinyl compounds and allyl compounds generally undergo this type of polymerisation. As majority of these monomers fall under the 'vinyl' category; hence, chain polymerisation is also customarily termed as 'vinyl polymerisation'.

Addition polymerisation consists of three important steps

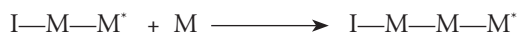
- (i) **Chain initiation** This step involves the formation of active molecules called chain initiators.

These chain initiators then attack the monomer to initiate the chain formation.





(ii) **Chain propagation** The initiated chain then attacks more monomeric molecules leading to the increase in the length of the chain.



Hence the polymeric chain propagates.

(iii) **Chain termination** The active centers are removed or they combine with each other and the chain propagation comes to an end.



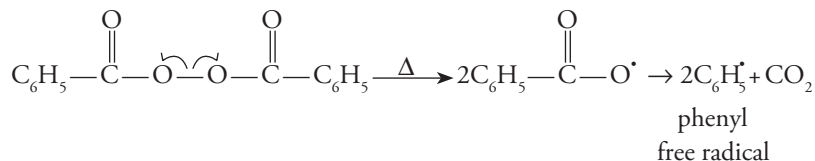
The addition polymerisation reaction can take place by three methods.

1. Free radical mechanism
2. Ionic mechanism (anionic and cationic)
3. Coordination mechanism

1. **Free radical addition polymerisation** It has three steps.

(i) **Chain initiation step** It involves the formation of free radicals in the initiation step.

The free radicals are formed as a result of homolytic dissociation of the initiator in the presence of heat, light or catalyst. Commonly used free radical initiators are azo compounds ($-\text{N}=\text{N}-$), disulphides ($-\text{S}-\text{S}-$), peroxides ($-\text{O}-\text{O}-$), hydroperoxides, peracids and peresters. An important example of a free radical initiator is benzoyl peroxide that dissociates as follows:

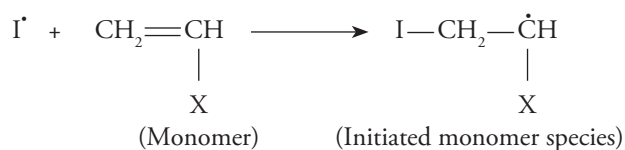


Here, half arrow (\curvearrowright) represents single electron shift. In $C_6H_5^\bullet$, the dot (\bullet) represents single electron.

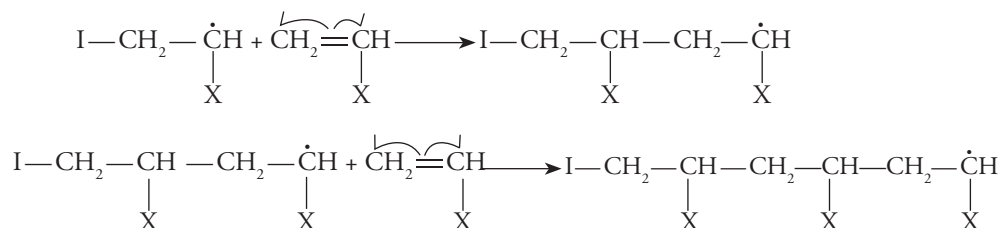
In general, the dissociation of the initiator (I—I) to form free radical species can be represented as



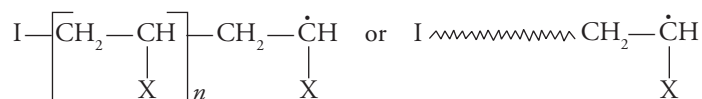
In the second step of initiation, a monomer molecule (M) is attached to the initiator radical. Considering vinyl as the monomer, this step can be represented as



- (ii) **Chain propagation step** In this step, the initiated monomer species adds additional monomer units as follows:

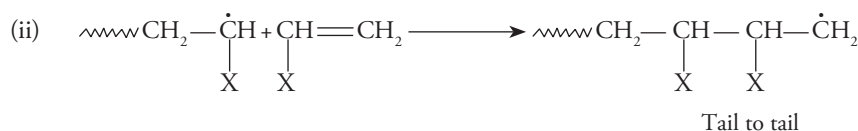
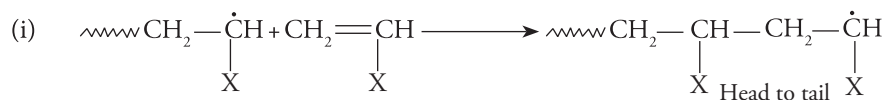


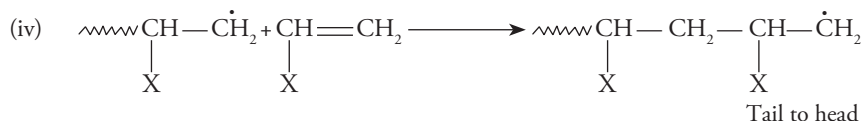
The propagation continues until the chain growth is stopped by some impurities or by termination process or till there is no further monomer left for attack. The structure of the growing chain can be represented as



n denotes the number of monomeric units added up in the chain growth and the wavy line also indicates the number of monomeric units added.

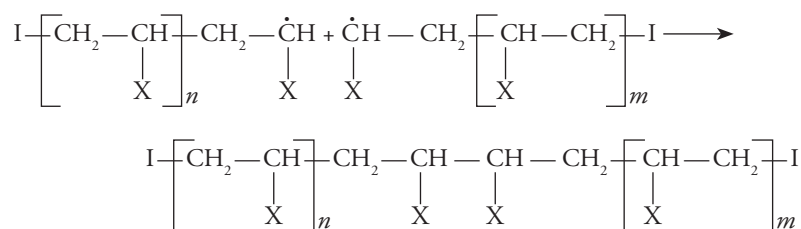
If the CH_2 part of monomeric chain is called head and CH_2X part is termed as tail, then four modes of addition can take place.





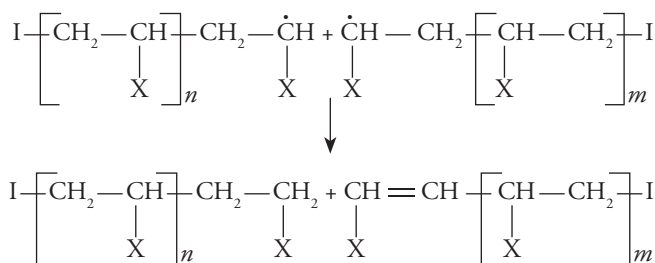
(iii) **Chain termination** This is the last step of polymerisation process where the growth of the chain is arrested. It can occur as follows.

- (a) **By combination of two growing chains (coupling)** As the decomposition of the initiator produces many free radicals at the same time, many chains are initiated and propagated simultaneously. The two growing chains can come close, collide and get deactivated.



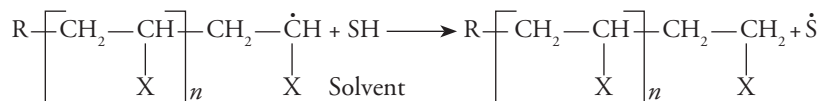
As this process involves the coupling of two lone pairs of electrons, this kind of termination is known as *termination by coupling*.

- (b) **By disproportionation** In this kind of chain termination, the hydrogen from one growing chain is abstracted by the other growing chain and results in the formation of two polymer molecules, one saturated and the other unsaturated. Contrary to the first type where a long-chain polymer is obtained, by this method we obtain two polymer molecules of shorter chain length.

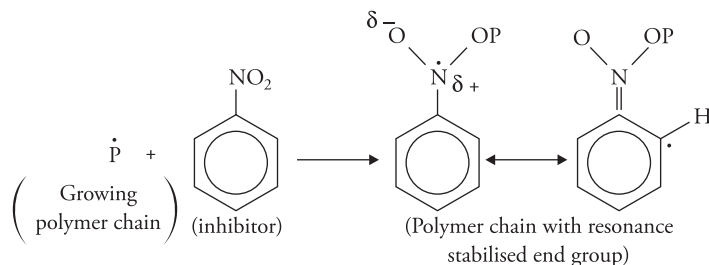


The products formed do not contain any reactive sites and may be termed as 'dead' polymer chain.

- (c) **Chain transfer** In this type of termination process, the growth of one polymer chain is stopped forming a dead polymer but there is simultaneous generation of a new free radical capable of initiating a fresh polymer chain growth. This reaction takes place by hydrogen abstraction from either solvent or some impurities present in the system.



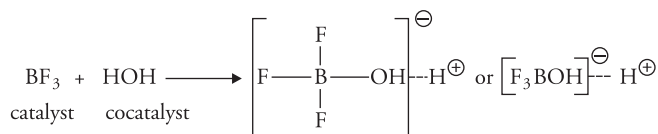
The chain can also be terminated by the addition of certain compounds, which are called inhibitors. Hydroquinone, nitrobenzene and dinitrobenzene are some of the commonly used inhibitors. Atmospheric oxygen is also a good inhibitor.



2. **Ionic addition polymerisation** Ionic polymerisations follow the same basic steps (initiation, propagation and termination). The chain is initiated either by a carbanion (C^\ominus) or carbocation (C^\oplus). Vinyl groups with electron-withdrawing groups polymerise by the anionic pathway, whereas vinyl groups with electron-donating groups can polymerise by a cationic mechanism.

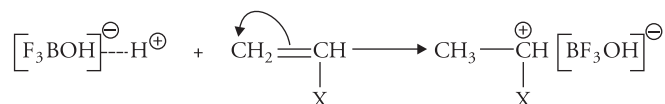
(i) **Cationic polymerisation**

- (a) **Chain initiation** Strong lewis acids like BF_3 and AlCl_3 are used as catalysts. Water exists as a co-catalyst to provide the proton.



where H^\oplus is the cationic initiator and $[\text{F}_3\text{BOH}]^\ominus$ is the counter ion.

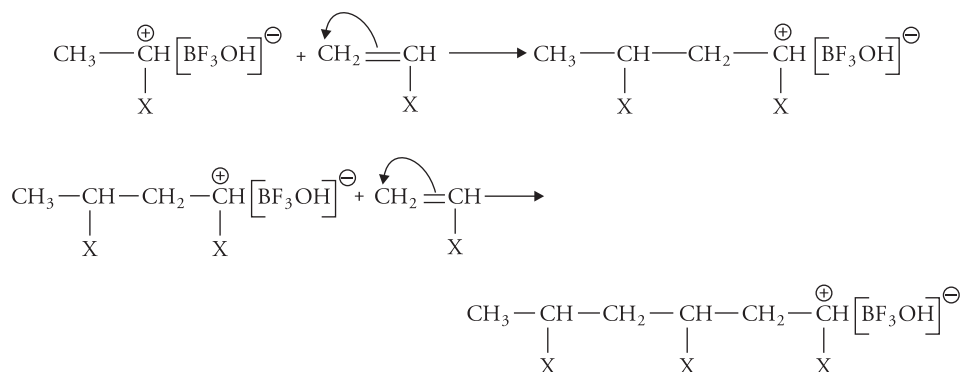
The H^\oplus ion now attacks the π -electron cloud of the monomer and a carbocation is formed.



where X = electron-donating group.

Chain propagation

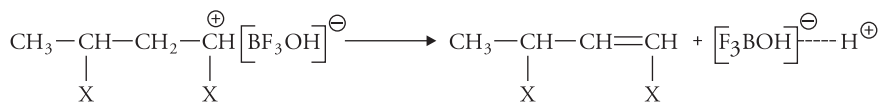
The chain initiator formed in the initiation step attacks new monomer units.



Chain termination

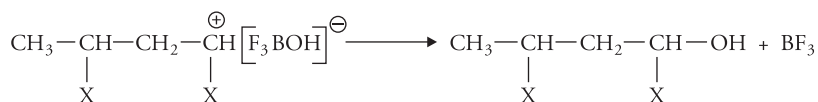
Chain termination can occur in two ways

- (a) Donation of proton to counterion by the growing chain resulting in the formation of a double bond at the end of the polymeric chain.



Thus, the initiator or catalyst is regenerated.

- (b) Formation of covalent bond between the carbocation and counter ion (coupling).



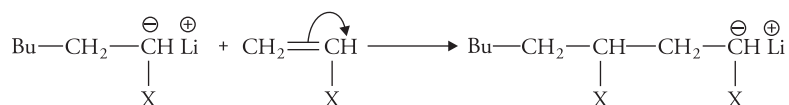
Again the catalyst BF_3 is regenerated. Monomers capable of undergoing cationic polymerisation are isobutylene, styrene, methyl styrene and many vinyl ethers.

(ii) **Anionic polymerisation**

Chain initiation Strong bases such as organoalkali compounds like n-butyllithium and ethylsodium initiate the anionic addition polymerisation.

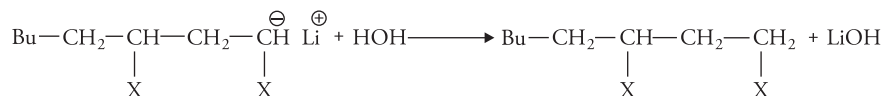


where X = electron-withdrawing group.

Chain propagation**Chain termination**

The termination in anionic polymerisation is not a spontaneous process. The polymerisation process continues till all the monomers are consumed.

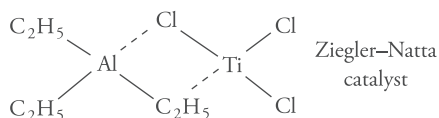
However, termination can be accomplished by transfer of negative charge to a species that is not directly involved in the reaction like CO_2 , methanol, water, etc.



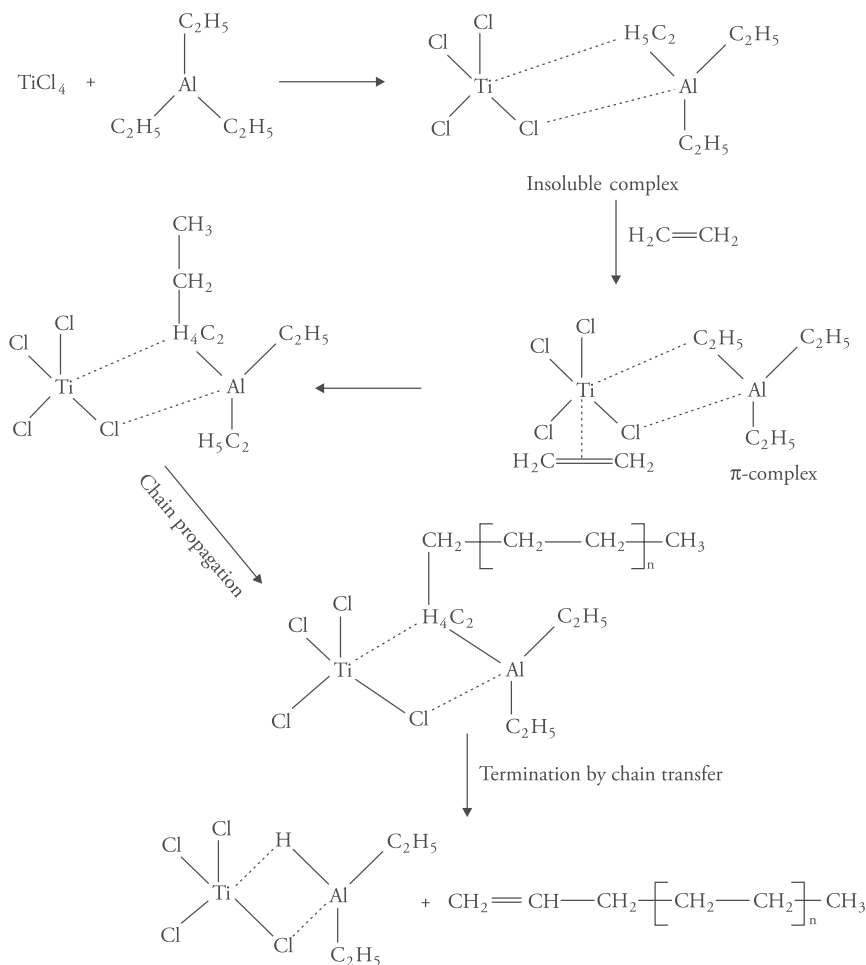
Monomers capable of undergoing anionic polymerisation are butadiene, isoprene, styrene and acrylonitrile.

3. **Coordination mechanism** These are polymerisation reactions taking place in the presence of organometallic compounds as catalysts.

Ziegler (1953) and Natta (1955) discovered that an organometallic compound in combination with transition metal halide (TiCl_4 and TiCl_3) can be used to prepare stereospecific polymers. The commonly used Ziegler–Natta catalyst is triethylaluminium in combination with titanium trichloride or titanium tetrachloride.

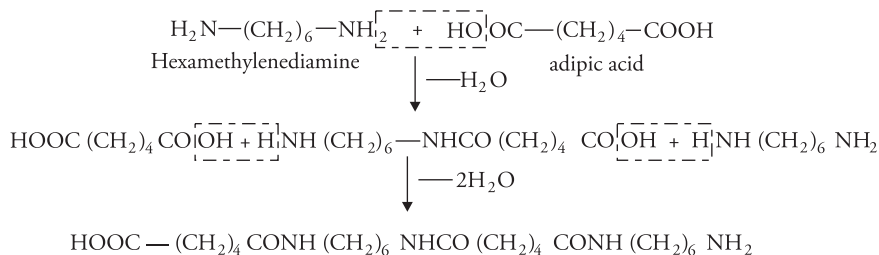


Mechanism of coordination polymerisation



Condensation polymerisation

Step polymerisation In condensation polymerisation, the polymerisation reaction proceeds step by step through reaction between the functional groups of the monomers with the removal of small molecules like water. For example, consider the formation of Nylon 6, 6:



The reaction proceeds step by step and the chain elongates.

6.5 Polymerisation Techniques

The various techniques of polymerisation are discussed below.

- (i) **Bulk polymerisation** Bulk polymerisation is simpler from the standpoint of formulation and equipment, but it is very difficult to control because the polymerisation is highly exothermic.

In this method, the monomer is taken in liquid state and the free radical initiator is dissolved in it. The chain transfer agent, used to control molecular weight, is also dissolved in the monomer. The homogenous reaction mixture is then heated or exposed to radiation for initiating the polymerisation. The mixture is stirred well because the reaction is highly exothermic. As the reaction proceeds, the viscosity of the medium increases and mixing becomes difficult. However, the polymer is insoluble in the monomer, polymer precipitates and the viscosity of the medium does not change appreciably.

Disadvantage The reaction mixture becomes viscous, the probability of chain collision becomes less and chain termination becomes difficult. Active radicals accumulate increasing the rate of polymerisation to such an extent that it may become uncontrolled and lead to explosion.

However, this method gives the polymer of highest purity because except chain initiator and chain transfer agents no other additive is used in the process.

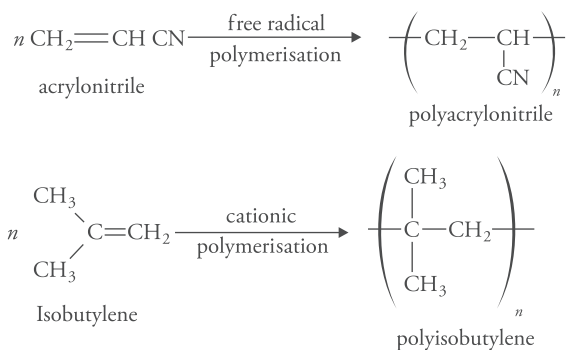
Bulk polymerisation technique is used in the polymerisation of methyl methacrylate or styrene and vinyl chloride.

- (ii) **Solution polymerisation** In this method, the monomer, free radical initiator and the chain transfer agent (whenever used) are dissolved in an inert solvent. The ionic or coordination catalysts are either dissolved or suspended. The polymer formed is in solution form. It is separated from solution either by evaporation of the solvent or by precipitation in a non-solvent. The inert solvent controls viscosity and promotes proper heat transfer.

Disadvantages

- (i) It is difficult to get high molecular weight polymers because no matter how inert the solvent is, chain transfer to the solvent cannot be completely ruled out.
- (ii) It is often difficult to remove the solvent completely from the finished polymer.

Solution polymerisation is used to manufacture polyacrylonitrile by free radical polymerisation and polyisobutylene by cationic polymerisation. Block co-polymers are also made exclusively by the technique.



(iii) Suspension polymerisation

This technique finds use in heterogeneous systems and is used only for water insoluble monomers. The monomer is first mechanically dispersed in a non-compatible liquid, usually water to form a suspension. The resultant monomer droplets are then polymerised using an initiator soluble in the monomer. The monomer is kept in suspension by continuous agitation and by the addition of stabilisers such as polyvinyl alcohol or methylcellulose. The polymer obtained is in the form of granular beads that are isolated by filtration or by spraying into a heated chamber (spray drying). As the polymer is granular in the form of beads or pearls, this method is also referred to as **beads or pearls polymerisation**.

Disadvantage This technique cannot be used for tacky polymers such as elastomers because of the tendency of agglomeration of polymer particles.

Suspension methods are used to prepare a number of granular polymers like polystyrene, styrene divinylbenzene beads (used for ion exchange resins), polymethylmethacrylate, polyvinylacetate, etc.

(iv) Emulsion polymerisation

This method was developed by Goodyear Tire and Rubber Company in the 1920s. Like suspension polymerisation, this technique also uses water as a dispersing medium. However, unlike suspension polymerisation, here the monomer is dispersed in the aqueous phase by an emulsifying agent such as soap or detergent. Redox type initiator radicals like hydrogen peroxide and persulphates are generated in the aqueous phase and they diffuse into soap micelles containing monomer molecules. As the polymerisation proceeds, more and more monomer migrates into micelles to continue the reaction. When new radical diffuses into the micelle, radical combination occurs and the polymerisation reaction is terminated. This method results in the formation of extremely high molecular weight polymers. Chain transfer agents are added to control the degree of polymerisation.

Emulsion polymerisation is widely used in industry for manufacturing water-based (latex) paints or adhesives in which the emulsified product is directly used. It is also used for preparing tacky polymers. Monomers such as vinyl chloride, butadiene, chloroprene and vinylacetate are polymerised by this technique.

6.6 Molecular Weight of Polymers

As the chain termination is a random process, all the polymeric chains formed are of different lengths. Under such a situation, it becomes difficult to express the molecular weight of the polymer. Hence, the molecular weight can be expressed as average of the molecular weights contributed by individual molecules present in the sample.

The molecular weight of a polymer is expressed in two ways.

(i) Number average molecular weight M_n

If n_1, n_2, n_3, \dots are the numbers of molecules with molecular masses M_1, M_2, M_3, \dots , respectively, then the number average molecular weight is

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\text{Total mass of the polymer sample}}{\text{Total number of molecules present in the sample}}$$

$$= \frac{\sum n_i M_i}{\sum n_i}$$

where n_i is the number of molecules or number of moles of molecules having molecular weight M_i .

Number average molecular weight can be measured on the basis of colligative property like osmotic pressure.

- (ii) **Weight average molecular weight** If m_1, m_2, m_3, \dots are the weights of species with molecular masses M_1, M_2, M_3, \dots , respectively, then the weight average molecular weight is

$$\overline{M}_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots}{m_1 + m_2 + m_3}$$

$$\overline{M}_w = \frac{\sum m_i M_i}{\sum m_i}$$

But $m_i = n_i M_i$

hence
$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

where n_i = number of molecules of mass M_i . \overline{M}_w is determined by methods like sedimentation, ultracentrifugation, etc.

Degree of polymerisation It represents the number of repeating units in a polymeric chain. For example, if a polymer has 5000 repeating units, then the degree of polymerisation is 5000.

Degree of polymerisation can be number average degree of polymerisation (\overline{DP}_n) or weight average degree of polymerisation (\overline{DP}_w).

$$(\overline{DP}_n) = \frac{\overline{M}_n}{M_0} \quad \overline{DP}_w = \frac{\overline{M}_w}{M_0}$$

\overline{M}_n = number average molecular weight

\overline{M}_w = weight average molecular weight

M_0 = molecular weight of monomer

Polydispersity index The ratio of mass average molecular mass to the number average molecular mass is called polydispersity index PDI.

$$\text{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

This gives an idea about the homogeneity of the polymer.

Solved examples

1. In a polymer sample, 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and the rest have 60,000. Calculate mass average and number average molecular masses.

Solution

$$\begin{aligned}\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{30 + 40 + 30} \\ &= 36000\end{aligned}$$

$$\begin{aligned}\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000} \\ &= 43333.\end{aligned}$$

2. There are two fractions with molecular weights 10^4 and 10^5 . Let us consider 100 g of the polymer, 10 g fraction has molecular weight 10^4 and 90 g has 10^5 . Calculate \overline{M}_w and \overline{M}_n .

Solution

$$\overline{M}_w = \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = \frac{10 \times 10^4 + 90 \times 10^5}{10 + 90} = 91000$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} = \frac{\frac{10}{10^4} \times 10^4 + \frac{90}{10^5} \times 10^5}{\frac{10}{10^4} + \frac{90}{10^5}}$$

$$n_1 = \frac{m_1}{M_1}$$

$$\frac{100}{\frac{100 + 90}{10^5}} = \frac{100 \times 10^5}{190} = 5.26 \times 10^4$$

Practice problems

1. Calculate the number average and weight average molecular mass of a polymer having
10 molecules of molecular mass each = 5000
20 molecules of molecular mass each = 7500

20 molecules of molecular mass each = 10,000

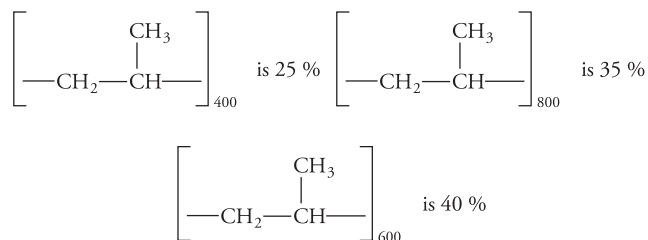
25 molecules of molecular mass each = 15,000

20 molecules of molecular mass each = 20,000.

5 molecules of molecular mass each = 25000

[Ans $\overline{M}_n = 13000$; $\overline{M}_w = 15,480$]

2. Calculate the number average and weight average molecular masses of polypropylene polymer with the following composition.



[Ans $\overline{M}_n = 25,565$; $\overline{M}_w = 27,084$]

6.7 Plastics

The term 'plastic' refers to the class of polymers that can be shaped into hard and tough utility articles by the application of heat and pressure.

They are strong, light, highly dielectric, durable and corrosion-resistant. Because of these properties, the use of plastics is increasing tremendously. Plastic materials are replacing metals in all walks of life. The reason for using plastics over metals is that

- They are light in weight and at the same time possess good strength, toughness and rigidity.
- They are corrosion-resistant and also resist the action of chemicals.
- They are less brittle than glass and can be made equally smooth and transparent.
- They do not absorb moisture.
- They can be easily moulded into desired shape.
- They can take a variety of colors, are heat-resistant and abrasion-resistant, and have good dimensional stability. Their maintenance cost is low.

Types of plastics Plastics are generally classified into two categories:

- Thermoplastics
- Thermosetting plastics

Thermoplastics They are plastic materials that soften on heating and can be moulded into desired shape. On cooling, they become hard. However, they can be resoftened and remoulded by the application of heat and pressure. The reason for resoftening of thermoplastic is that they are composed of linear or long-chain molecules. On heating the intermolecular bonds weaken, the material softens and thus can be moulded again without any damage.

Common examples of thermoplastics are polyethene, polypropylene, polystyrene, teflon, polyamides, etc.

Thermosetting plastics They are those plastic materials that, when subjected to heat and pressure, change into a hard and rigid substance. Once they set, they cannot be softened again by the application of heat. The reason is that during moulding they acquire three-dimensional cross-linked structure. Such three-dimensional polymers will not soften when heated but may decompose or disintegrate at high temperatures.

Common examples are bakelite, melamine formaldehyde, epoxy resins, etc.

Table 6.1 Difference between the thermoplastics and thermosetting plastics

Thermoplastics	Thermosetting plastics
1. Once moulded, they can be resoftened and reused	Once moulded, they set permanently. They do not soften again on heating
2. They are softer and less strong. The polymeric chains are held together by weak van der Waals forces	They are strong and hard. There are cross-linkages and covalent bond formation between the adjacent polymeric chains
3. They are generally formed by addition polymerisation reaction	These are formed by condensation polymerisation reaction
4. As they soften again and again, they can be recycled, reused and reclaimed from waste	They cannot be recycled, reused or reclaimed from waste
5. Examples include polythene, polypropylene, teflon, nylon, natural rubber	Examples include bakelite, melamine formaldehyde, epoxy resins, vulcanised rubber

Moulding constituents of a plastics During moulding, different constituents are added to impart the required property. These constituents that are added to plastics during its moulding process are termed as its *moulding constituents*. The main compounding ingredients and their functions are given below.

1. **Resin** These are substances that hold the different constituents together. Usually thermosetting resins are used.
2. **Plasticisers** These materials increase the plasticity and flexibility. They neutralise the intermolecular forces of attraction and impart greater freedom of movement between the polymeric macromolecules. Commonly used plasticisers are vegetable oils, camphor, esters (of stearic, oleic or phthalic acids) and phosphates like tricresyl phosphate.

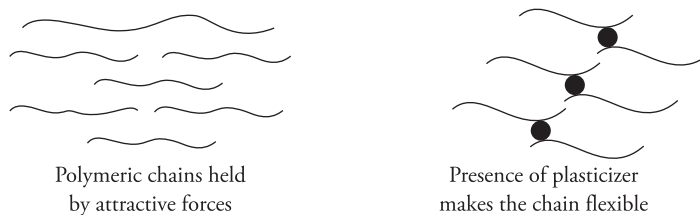


Figure 6.2 Effect of plasticiser on the polymer chain

3. **Fillers** These are added to improve the hardness, tensile strength, opacity and workability of the plastic. Fillers impart special characters to products. For example, addition of carbon black to natural rubber increases its tensile strength and makes it abrasion-resistant, addition of asbestos to a plastic material provides heat and corrosion resistance, addition of barium makes the plastic impervious to X-rays, whereas quartz, mica and carborundum are added to provide extra hardness.
4. **Lubricants** Lubricants like waxes, oils and soaps prevent the plastic material from sticking to the mould. They also impart flawless, glossy finish to the final products.
5. **Catalysts or accelerators** They are added to accelerate the polymerisation process. They are particularly used for thermosetting plastics. Commonly used catalysts are hydrogen peroxide, benzoylperoxides, metals like Ag, Cu and Pb and oxides like ZnO.
6. **Stabilisers** They improve the thermal stability during processing. Stabilisers are added to those polymers which have a tendency to decompose at moulding temperature. For example, vinyl polymers. Commonly used stabilisers are salts of lead and stearates of lead, cadmium and barium.
7. **Coloring materials** Organic dye stuffs and opaque inorganic pigments are commonly used to impart color to the plastic products.

Plastic moulding processes Plastic materials supplied in granular, powder or other forms are moulded into articles by various methods. The commonly used methods are as follows:

- (a) Compression moulding
 - (b) Transfer moulding
 - (c) Injection moulding
 - (d) Blow moulding
 - (e) Extrusion moulding
- (a) **Compression moulding** Compression moulding is widely used to produce articles from thermosetting plastics. It is used for manufacturing electrical parts such as switches, switch boards, cooker handles, etc. The mould used for the purpose is made up of two halves. The upper half has a projection and is called the male die, whereas the lower half called the female die has a cavity.

The material to be moulded is placed in the lower female cavity and is heated continuously by steam or electricity. The movable bolster is raised so that the female mould portion contacts the male die, which is also heated. As the mould closes down under pressure, the excess material flows out of the mould as *flash*. Under the influence of heat, the compacted material gets cured and hardened. The mould is opened while it is still hot to release the moulded product.

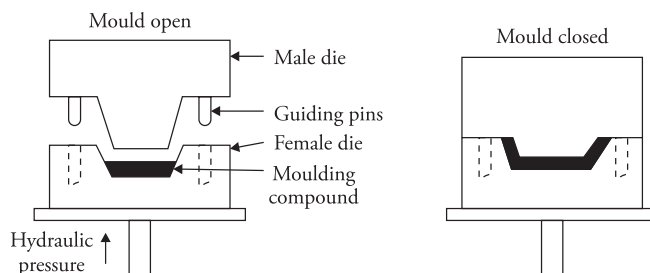


Figure 6.3 Compression moulding

- (b) **Transfer moulding** It is used for moulding thermosetting materials. Unlike compression moulding, the moulded material in transfer moulding is preheated and loaded into a chamber known as the pot. A plunger (piston) forces the molten material into the mould cavities through channels known as *sprue and runner system*. The mould remains closed as the material is inserted. The molten material sets, gets cured and is released by opening the mould. The moulds in both compression and transfer moulding remain closed till the curing reaction within the material is complete. Transfer moulding, unlike compression moulding, uses closed mould.

Transfer moulding differs from compression moulding as in transfer moulding heated, molten resin is inserted in the mould, whereas in compression moulding granular or powdered resin is placed in the mould, which is then heated and pressure is applied. No further pressure is needed in transfer moulding.

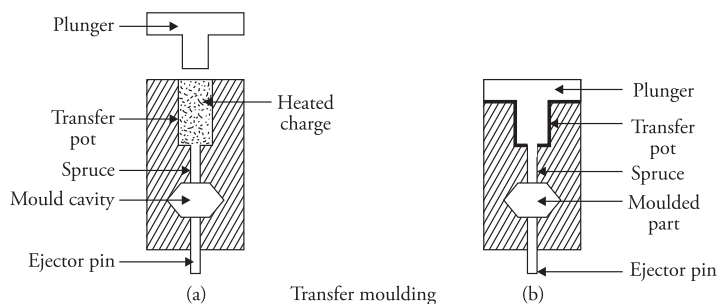


Figure 6.4 Transfer moulding

- (c) **Injection moulding** It is used for producing articles made of thermoplastic materials like mugs, buckets, dust bins, chairs, etc.

The mould consists of a two-part system; one part is movable and the other is stationary. The stationary part is fixed to the end of the cylinder, whereas the movable part can be opened or closed on to the stationary part.

In this process, a correct amount of plastic material as granules, pellets or powder is fed from the hopper into the cylinder. The piston pushes the plastic material into the heating chamber where it melts to form a viscous liquid. Again with the help of the piston the molten plastic material is injected through the nozzle into the mould cavity. Pressure is maintained in the mould cavity. The material is cooled by water circulation. It solidifies. Finally, the mould is opened, the piece is ejected, the mould is closed and the entire cycle is repeated. The most outstanding feature of this technique is the speed with which the pieces may be produced.

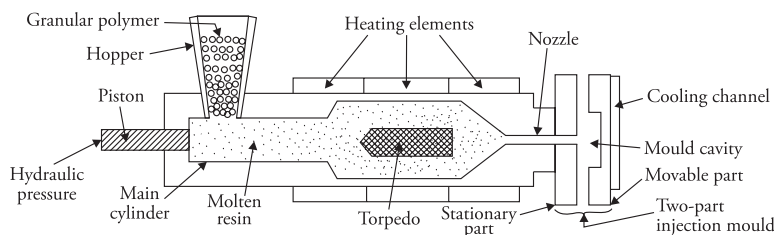


Figure 6.5 Schematic diagram of injection moulding machine

- (d) **Blow moulding** It is used for producing hollow articles like bottles and hollow toys. Thermoplastic articles such as PE, polycarbonate, PVC, nylon and styrene are blow-moulded.

In this process a hot, softened thermoplastic tube called 'parison' is properly placed inside the two-piece hollow mould. The split mould is then closed, sealing the bottom. This joint is usually seen at the bottom of the plastic bottles. Air is then blown in the hot parison. It is inflated and acquires the shape of the mould. The mould is allowed to cool and the rigid thermoplastic article formed is removed by opening the mould.

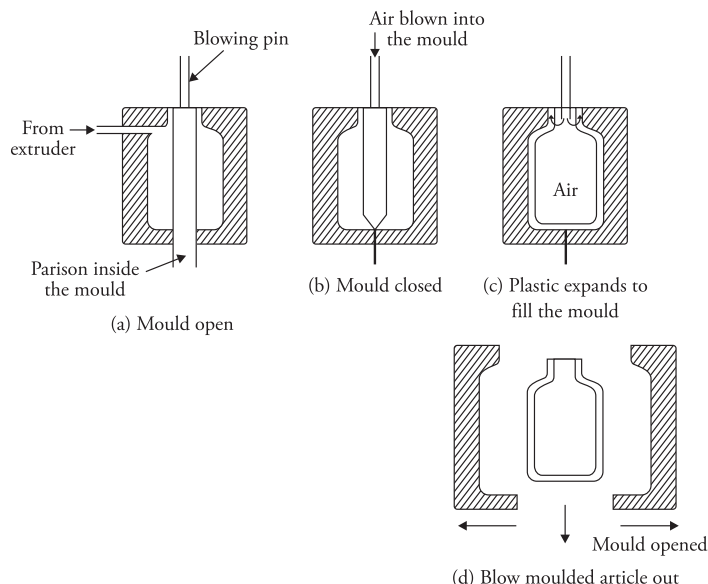


Figure 6.6 *Blow moulding*

- (e) **Extrusion moulding** This method is used for making elongated and continuous articles such as rods, pipes, tubes, hose pipes films, filaments and sheets. An extruder resembles the injection moulding apparatus, except that the mould cavity is replaced with a die.

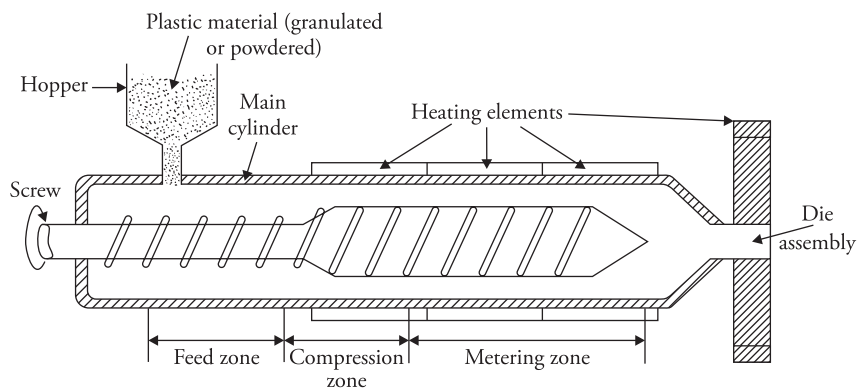


Figure 6.7 *Schematic diagram of extrusion moulding machine*

In this process, the compounded plastic material in the form of powder or granules is fed into the electrically heated cylinder using a hopper. A helically rotating screw inside the cylinder further works the plastic charge. During the journey from hopper to the die, the plastic material passes through three zones namely feed zone, compression zone and metering zone. The feed zone receives the charge from the hopper. No heating takes place in the feed zone. In the compression zone, the powdered charge melts because of heating and compression by the moving screw. The pasty molten mass enters the metering zone. The pressure in this region enables the molten polymer to enter the die and come out of it with the desired shaped. The material extruded out of the die is quite hot (usually 125–350 °C) and is carried over the conveyor belt through a tub containing cold water.

The process of extrusion is also used for coating wires and cables with PVC or rubber. This method gives products of good surface finish and dimensional stability.

This process is widely used to encapsulate or enclose items such as coils, plugs, integrated circuits, utensil handles, etc.

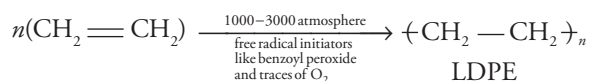
6.8 Individual Polymers

Addition polymers

1. **Polyethylene** Also known as polyethene, it is an important thermoplastic resin prepared by the addition polymerisation of ethylene. It is of several types

(a) Low-density polyethene

Preparation It is prepared by the polymerisation of ethylene at high pressure (1000–3000 atmospheres) at 250 °C in the presence of free radical initiators like benzoyl peroxide. Traces of oxygen catalyse the reaction.



Properties It is a waxy solid that floats on water and has a linear branched structure. The branches do not allow the chains to pack efficiently; hence, its density is low (0.91–0.925 g/cm³). It is not polar and has weak intermolecular forces. It is tough, flexible, chemically inert and has excellent electrical insulation properties.

Applications Low-density polyethene (LDPE) is used for storing a variety of foodstuffs. It is used for making carrier bags, films for general packing, moulded toys, mugs and ink tubes for pens.

(b) High-density polyethene

Preparation

- (i) Ethylene is polymerised under 6–8 atmospheric pressure at 60–70 °C in the presence of Ziegler–Natta catalyst (triethylaluminium and titanium tetrachloride).
- (ii) At 35 atmospheric pressure, 60–200 °C temperature and in the presence of metal oxide catalyst like CrO₃ supported on silica alumina, ethylene polymerises to give high-density polyethene (HDPE).

Properties The polymeric chains are linear and hence they pack easily. Hence, it has high density ($0.95\text{--}0.97\text{ g/cm}^3$). It is more stiff, hard and has greater tensile strength compared with LDPE. Its softening temperature is high ($135\text{ }^\circ\text{C}$). It has excellent electrical insulation properties, has low water and gas permeability, has excellent chemical resistance and is free from odor and toxicity.

Applications

It is used for making insulations, pipes, bottles for milk, household chemicals and drug packing. It is also used for the manufacture of crates, industrial containers and overhead tanks. HDPE sheets are used for packing materials and for making toys.

(c) LLDPE (linear low-density polyethylene) It is actually a copolymer of ethylene and 1-butene (with lesser amounts of 1-hexene and higher 1-alkenes to vary the density) manufactured with Ziegler-type catalysts. First marketed in the 1970s, LLDPE is attractive because it requires considerably less energy to produce than LDPE.

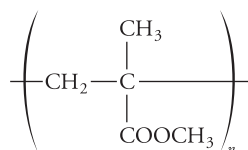
Uses It is used in making golf ball covers, orthopaedic devices, blending with LDPE, packing films and bottles.

(d) UHMWPE (ultrahigh molecular-weight polyethylene)

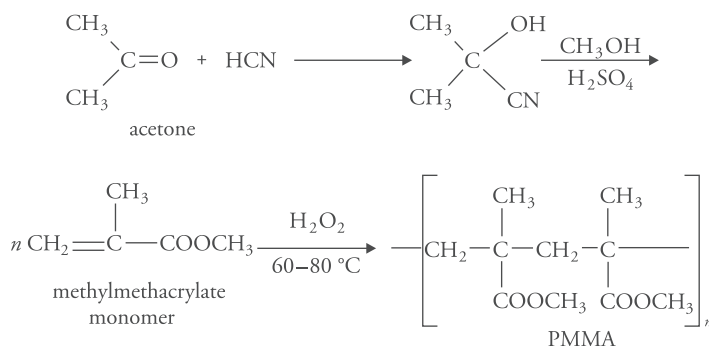
Uses It is used in making surgical prostheses, machine parts, heavy-duty liners.

Polymethylmethacrylate (PMMA)

The polymethylmethacrylate polymer has the following structure:



It is manufactured by the polymerisation of methylmethacrylate monomer in the presence of free radical catalyst hydrogen peroxide at $60\text{--}80\text{ }^\circ\text{C}$. The mechanism is as follows:



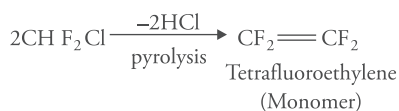
Properties It is also known as plexi glass. It is colorless, transparent, amorphous and has good strength.

Although chemically inert, it dissolves in organic solvents such as ketones, chlorinated hydrocarbons and esters.

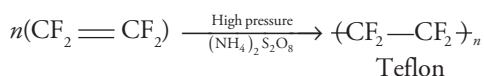
Applications

Its optical transparency is better than that of glass. Hence, it is an excellent substitute for glass. It is used for the manufacture of contact lens, spectacles and windscreens. Because of its good mechanical properties it is used for the manufacture of cockpit canopies, attractive signboards and for decorative purposes. It has high weather resistance. It does not turn yellow or crumble when exposed to sunlight. It is used for making transparent windows, aquariums, tail-lights of automobiles, bathtub liners, sinks, cell phone display screens and so on.

Teflon (polytetrafluoroethylene, PTFE) Its trade name is teflon. It is prepared by the polymerisation of tetrafluoroethylene at high pressure in the presence of ammonium persulphate as catalyst.



The monomer is polymerised using ammoniumpersulphate as initiator.



Properties

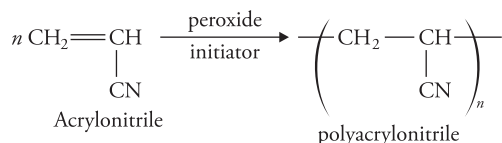
It is a linear polymer with practically no branching. It has high mechanical strength and is chemically inert. Its softening temperature is high (350 °C). It does not dissolve in acids, including fuming nitric acid, and is also resistant to the attack of corrosive alkali and organic solvents.

Applications

It is used for making articles like pump valves and pipes where chemical resistance is required. It is used for manufacturing insulations for motors, transformers, capacitors, electrical cables, etc. It is also used for making gaskets, gas seals, non-sticking stopcocks for burette and for making teflon-coated non-stick utensils.

Polyacrylonitrile (PAN)

Also known as orlon or acrilon, it is produced by the radical polymerisation of acrylonitrile (vinyl cyanide) using peroxide initiators. The chemical reactions involved are as follows:

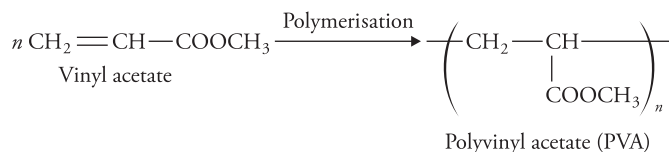


Properties It has high heat resistance (softening temperature 220 °C) and exhibits good mechanical properties. It is soluble in solvents like dimethyl formamide, dimethylsulphoxide, etc.

Applications It is used to produce PAN fibres that find use in making blankets, sweaters, bathing suits, synthetic carpets, etc. On copolymerisation with butadiene, it produces nitrile rubber (Buna-N), which is of great industrial importance.

Polyvinylacetate (PVA)

It is obtained by heating vinyl acetate in the presence of small amount of benzoylperoxide.



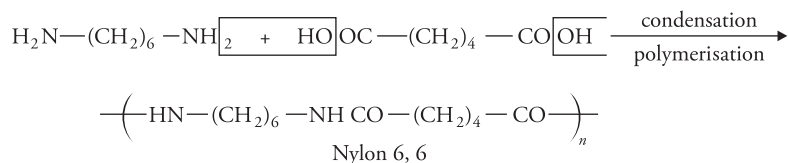
The polymer can be prepared by bulk, emulsion or solution polymerisation methods.

Properties PVA is a solid resin that is insoluble in water but is soluble in aromatic solvents and also in alcohols and esters. It is saponified with great difficulty and is not absorbed by the digestive system. It is resistant to atmospheric air, water and chemicals.

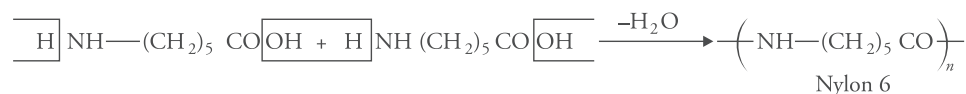
Uses It is used in adhesives, lacquers, paints and for large-scale manufacture of gramophone records. Polyvinyl acetate adhesives are used for bonding textile to textile, leather to leather, paper to textile, etc. Polyvinyl acetate is used as a basic material for chewing gums and surgical dressings. On copolymerisation with polyvinyl chloride, it is converted into a soft polymer, vinylite, which is used as a surface-coating material for metals. Polyvinyl acetate is mainly used for the manufacture of polyvinylalcohol.

Condensation polymers

Nylon They are polyamide polymers having recurring amide groups. Nylon 6, 6 is formed by the condensation of hexamethylenediamine and adipic acid.

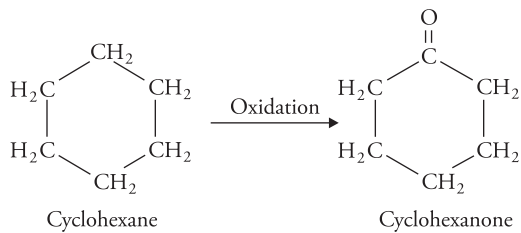


Nylon 6 It is produced by the self-condensation of ϵ -aminocaproic acid.

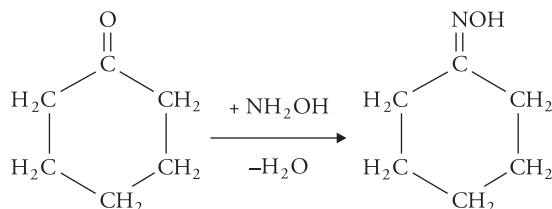


The various steps for the synthesis of nylon-6 starting from cyclohexane are as follows:

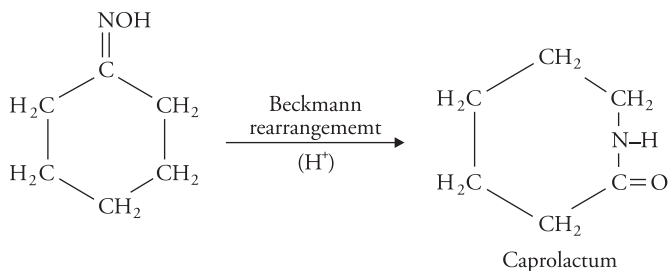
Step (i) Conversion of cyclohexane to cyclohexanone by oxidation.



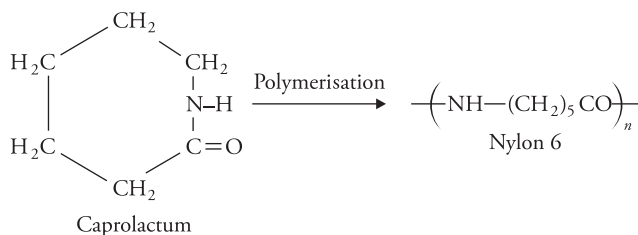
Step (ii) Cyclohexanone reacts with hydroxylamine NH_2OH to form cyclohexanone-oxime.



Step (iii) Conversion of cyclohexanone-oxime into caprolactum by Beckmann rearrangement in the presence of H_2SO_4 .

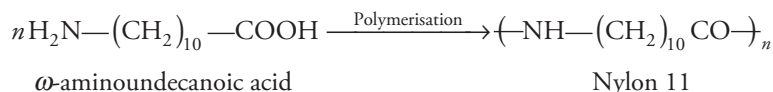


Step (iv) Ring opening and polymerisation of caprolactum to give nylon-6.



Nylon-11

It is prepared by the self-condensation of ω -aminoundecanoic acid.

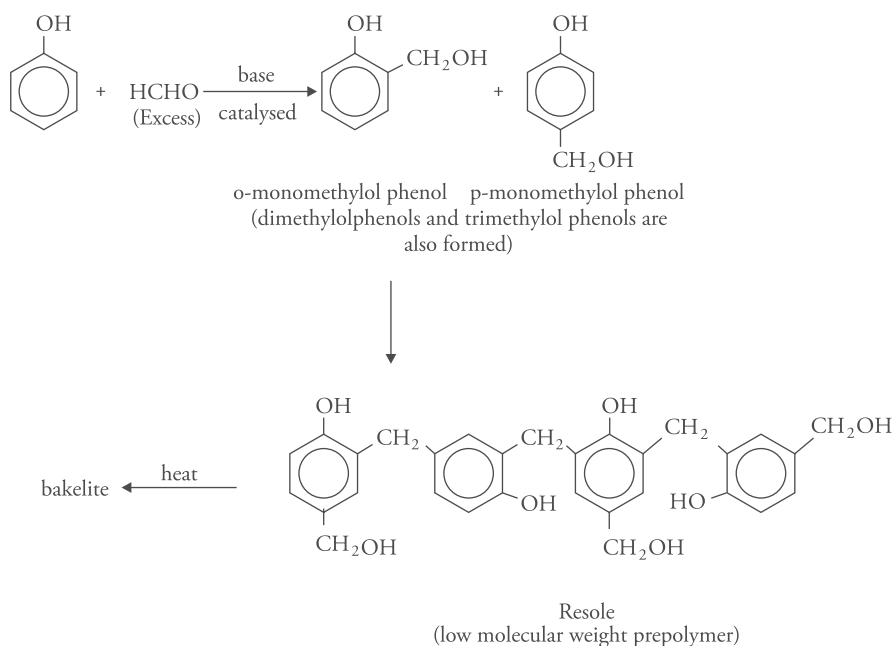


Properties It is a linear polymer. The polymeric chains are held together by hydrogen bonding. They are translucent, high-melting polymers known for their toughness, abrasion resistance, elasticity and high crystallinity.

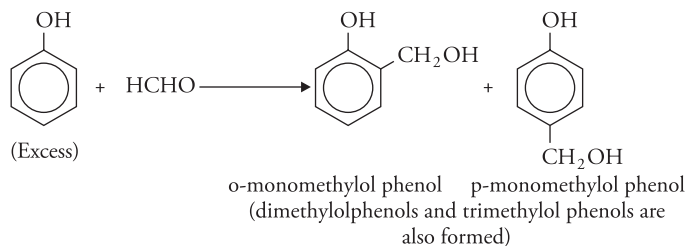
Applications Nylon 66 is used for making fibres that are used for making socks, undergarments, carpets, etc. It also finds use in mechanical engineering for the manufacture of gears, bearings, bushes, electrical mountings. Nylon moving parts work quietly without any lubrication. Nylon 6 is mainly used for making tyre cords. Bristles, brushes are generally made of Nylon 6, 10. Nylon 11 and Nylon 12 are used for making flexible tubings for conveying petrol. Glass-reinforced nylon plastics find use in domestic appliances, radiator parts of cars, etc.

Phenol formaldehyde resin (bakelite) Commercially known as bakelite, this polymer is formed by the condensation of phenol and formaldehyde in the presence of acidic/alkaline catalyst. They are also known as phenoplasts and PF resins. Phenol-formaldehyde resins are normally prepared by two different methods.

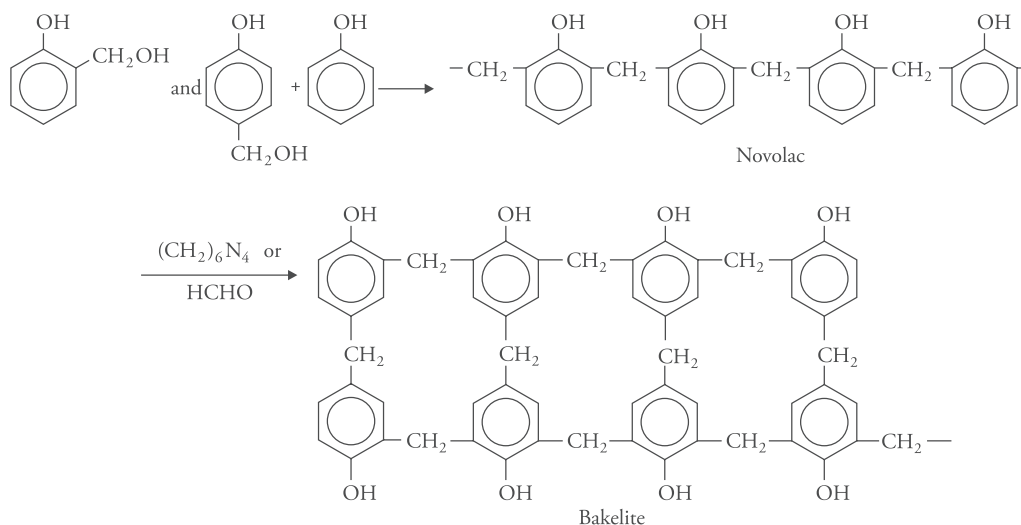
- (i) Base catalysed using excess of formaldehyde over phenol. The initially formed product called 'resole' changes into thermosetting polymer 'bakelite' simply by heating.



(ii) Acid catalysed method using excess of phenol.



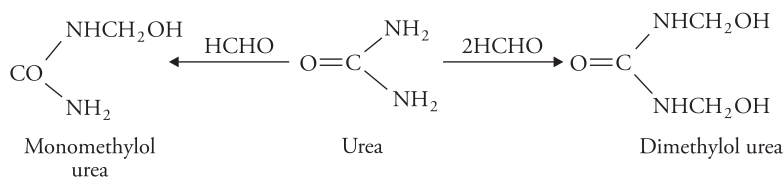
These undergo condensation to form a linear prepolymer novolac. Unlike resole, novolac contains no residual hydroxymethyl groups. Bakelite is obtained by heating novolac with formaldehyde, paraformaldehyde or hexamethylenetetramine (it produces HCHO).



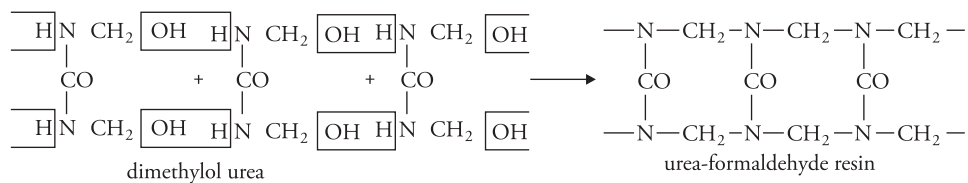
Properties Phenolic resins are hard, rigid, strong with excellent heat, moisture, chemical and abrasion-resistance. They are scratch-resistant and possess excellent electrical insulating properties.

Applications They are used for making domestic switches, plugs, handles for pressure cookers, saucepans and frypans. They are also used for making moulded articles like telephone parts, cabinets for radio and television. They find use as adhesives for grinding wheels and brake linings. They are used in paints and varnishes, in the production of ion-exchange resins for water-softening and for making bearings used in propeller shafts for paper industry and rolling mills.

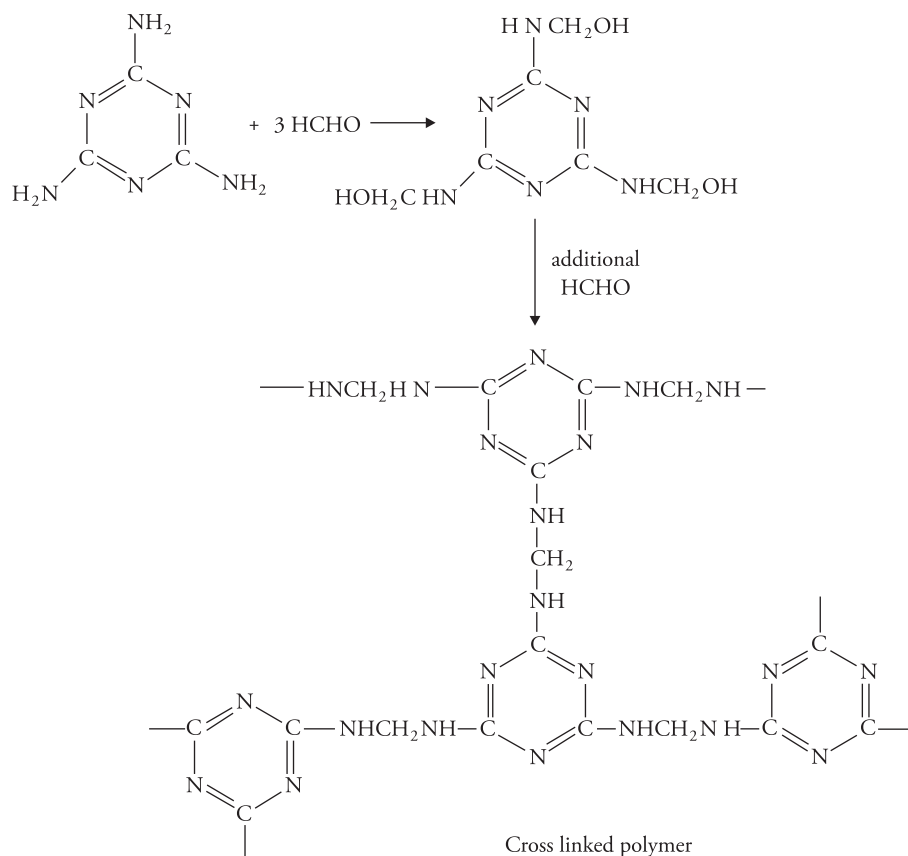
Urea-formaldehyde resin and melamine formaldehyde resin They are obtained by the reaction of urea or melamine with formaldehyde. Two parts of urea and one part of formaldehyde react in a stainless steel vessel in a basic medium at about 50 °C to give mono and dimethylol urea.



These methylol derivatives are compounded with fillers, plasticisers, pigments, etc., and then cured by applying heat and pressure. During curing, cross-linked urea-formaldehyde polymer is formed.



Melamine and formaldehyde also react to give methylol derivatives of melamine.

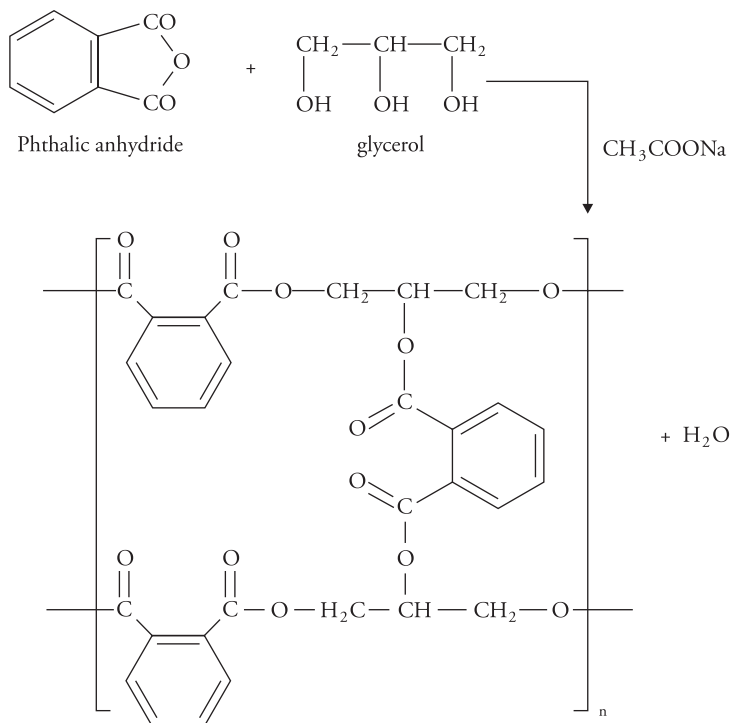


Properties Their tensile strength and hardness is better than phenolic resins. However, heat and moisture resistance are low.

Applications They are used for the preparation of lacquers and in the manufacture of decorative laminates.

Glyptal

Glyptal is a cross-linked, thermoset polyester. It is prepared by condensing glycerol (a triol with phthalic anhydride)



Glyptal

During polymerisation, the monomers join to form large molecules and because of increased attractive forces between the molecules the mixture becomes viscous.

Properties Glyptal is harder and more brittle than the linear polyesters. It does not soften when heated. The cross-linking keeps the polymer chains from moving with respect to one another when heated. It is a fast drying thermoplastic that can bond a variety of materials. It has strong, durable bonds that have excellent resistance to oil, gasoline and moisture.

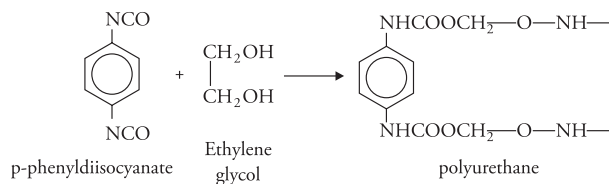
Uses Glyptal and other alkyd polyesters are useful as coating materials and are not used for making fibres and plastic products. Glyptal was first commercialised in 1902 for use in paints and varnish industry. Glyptal is added in paints to improve their washability and adhesion. Its fast drying time along with its good dielectric strength makes it an excellent general-purpose adhesive for many electrical and non-electrical applications. It is also used as a sealing wax.

Polyurethanes Polyurethanes were developed by Otto Bayer and co-workers in 1937.

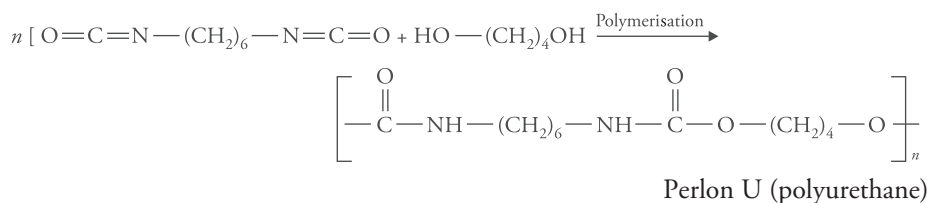
They are characterised by the presence of urethane group —N—C—O linkage.



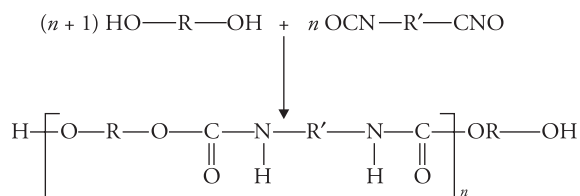
They are obtained by condensing di-isocyanate and diol. When ethylene glycol reacts with p-phenyldi-isocyanate polyurethane is formed.



1, 4-butanediol and 1,6-hexanediisocyanate react to yield Perlon- U (a crystalline polymer).



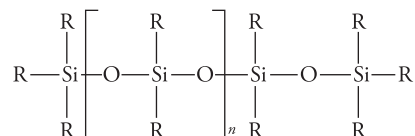
General reaction



Properties They have high strength; good resistance to gas, oil and aromatic hydrocarbons; high abrasion resistance; excellent resistance to oxygen and ozone, but are susceptible to microbial attack. They are also less stable at high temperatures.

Applications Polyurethanes are used to make foams used in cushions for automobiles and furniture, they are also used for coatings, as adhesives and as elastomers. Polyurethane fibres are used for making swimsuits. They also find use in the manufacture of shoe soles, solid tyres and impellers.

Silicone resins They are inorganic polymers containing alternate silicon–oxygen structure. Organic radicals are attached to the silicon atoms.



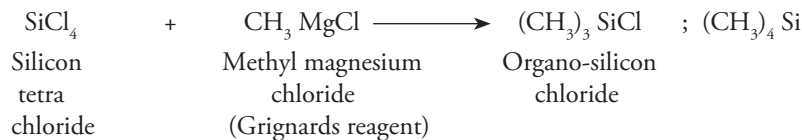
where R = alkyl or phenyl radical.

Preparation

(i) By the reactions of alkyl halide with silicon.

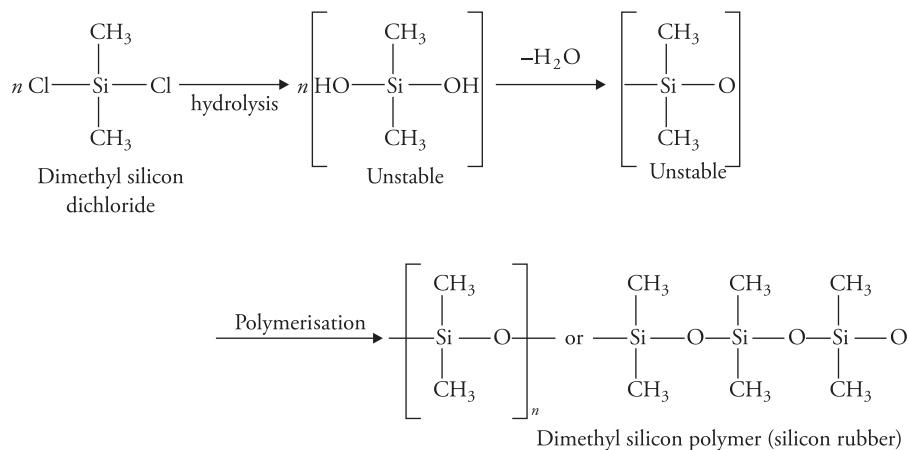


(ii) Reaction of silicon halide with Grignard's reagent

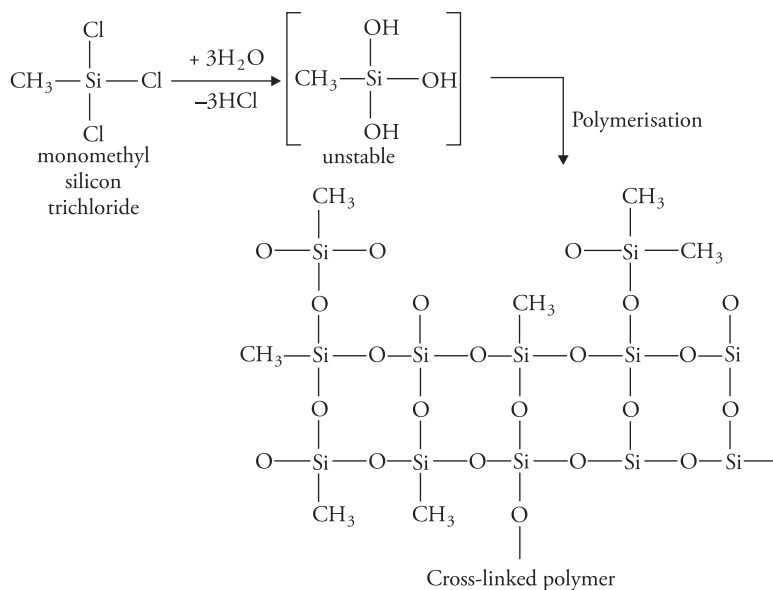


Mixture of organosilicon chlorides is obtained, which is separated by fractional distillation and polymerised by controlled hydrolysis.

1. Dimethyl-silicon dichloride yields long-chain polymer as it is 'bifunctional'.



2. Monomethylsilicontrichloride yields a cross-linked polymer as it is trifunctional.



Properties Silicones are water repellent and chemically inert. They are resistant to oxidation, thermal decomposition and attack by organic reagents. They are also good electrical insulators and antifoaming agents.

Uses Their viscosities do not change with temperature; hence, they are used for making all weather lubricants. They are used for coating papers, textiles and wools to make them water-proof. They are used as antifoaming agents in industries. Silicones are also added to paint for resisting dampness and for water-proofing. Owing to their water-repellant nature and high dielectric constant, they also find use in electrical condensers.

6.9 Rubbers (Elastomers)

The American Society for Testing and Materials (ASTM) defines an elastomer as ‘a polymeric material that at room temperature can be stretched to at least twice its original length and upon release of stress it will return immediately its original length.’

As rubbers can be stretched to 4–10 times of their original length and return to their original length as soon as the stretching force is removed, they are also termed as elastomers. The terms ‘rubber’ and ‘elastomers’ are used interchangeably and refer to polymers that exhibit resilience, or the ability to stretch and retract rapidly.

The elastic deformation in an elastomer arises from the fact that under unstressed condition an elastomer molecule is not straight-chained but is in the form of a coil. Hence, unstretched rubber is amorphous (the polymeric chain is randomly entangled). As soon as it is stretched, the polymer chain tends to straighten and becomes aligned. This increases its crystallinity and decreases the entropy (as it becomes ordered). Hence, as soon as the stretching force is removed, it again reverts back to its original coiled state so that the material becomes amorphous, its randomness or entropy increases and it acquires a stable state.

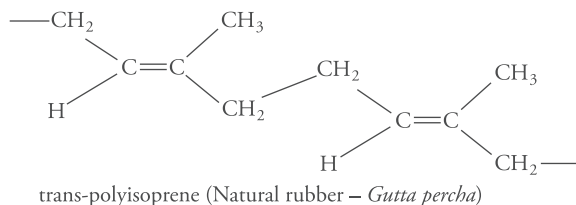
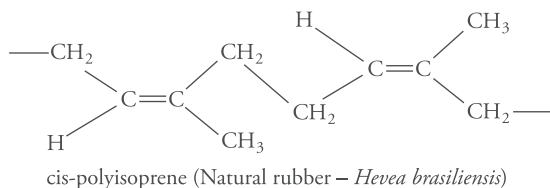
Natural rubber

The term *rubber* was coined by Joseph Priestley when he noted that it could be used to *rub* pencil marks. It is obtained from the bark of a tree (*Hevea brasiliensis*) that grows wildy in South America. Natural rubber consists of 97% cis-1, 4 polyisoprene. To obtain rubber from the Hevea tree, incisions are made in the bark of the rubber tree. The milky latex that flows out is collected in small vessels and then sent to the factories for treatment. The latex is an aqueous suspension of about 32–35% rubber and about 5% other compounds including fatty acids, sugars, proteins, sterols, esters and salts. It is coagulated with acetic acid or formic acid and filtered. It is then bleached with sodium bisulphite (NaHSO_3), washed and dried. The rubber is converted into a soft gummy mass, which is then passed through a creping machine with (having two rollers about 3 mm apart and 50 cm wide) longitudinal grooves. A sheet having rough surface is obtained. It is dried in air at 50 °C. This is called crepe rubber.

To obtain **smoked rubber**, thicker sheets are obtained by passing first through a series of smooth rollers and then finally through a roller to give it a ribbed pattern. The sheets are then hung in smoke houses and dried at 40–50 °C by burning wood or coconut shells.

Rubber can also be obtained from the mature leaves of *Gutta percha*. It is recovered by solvent extraction. It can also be obtained by grinding the mature leaves and treating them with water at

70 °C for half an hour and then pouring them into cold water. The rubber floats on the water surface and is removed. Chemically, it is trans-1, 4-polyisoprene.

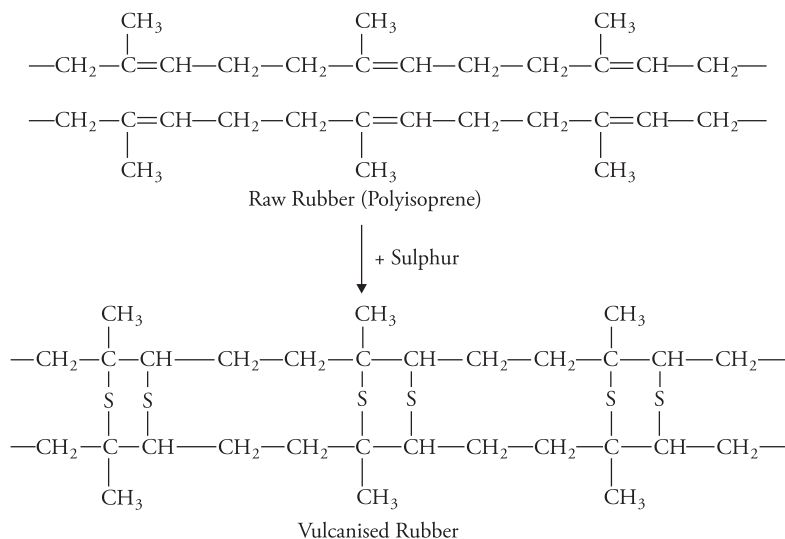


Properties of natural rubber

1. Natural rubber is a tough elastic material that softens on heating.
2. It hardens at 5 °C.
3. It becomes tacky at 30 °C (i.e., when two pieces of rubbers are pressed together, they coalesce to form a single piece).
4. It oxidises to a sticky mass on exposure to sunlight.
5. It is soluble in organic solvents.
6. It has large water absorption capacity.
7. It is plastic in nature and undergoes permanent deformation when stretched chains slip past each other and then get separated resulting in the breakage of the rubber.
8. It is weak and has low tensile strength (200 kg/cm²).
9. It is non-resistant to vegetable oils, minerals oils, gasoline, benzene and carbon tetrachloride.

Vulcanisation

It was developed by Charles Goodyear in the year 1839. When natural rubber is heated with sulphur or other suitable reagents, a non-reversible chemical reaction occurs. Cross-linkages are formed between the adjacent polymeric chains and natural rubber (a thermoplastic) changes into a cross-linked polymer (a thermoset). The following reaction occurs:



Advantages of vulcanisation

Vulcanisation transforms a weak elastomer into a strong, elastic and tough rubber. It improves the tensile strength, stiffness, durability, elasticity, chemical resistance, resistance to changes in temperature and tackiness remarkably. Its water absorption capacity reduces greatly. Vulcanised rubber has better insulation properties than raw rubber. Ebonite (32% sulphur) has extremely good insulating properties. Resilience (tendency of an elastomer to return to its original shape on the release of stress) of vulcanised rubber improves manifolds as compared with raw rubber.

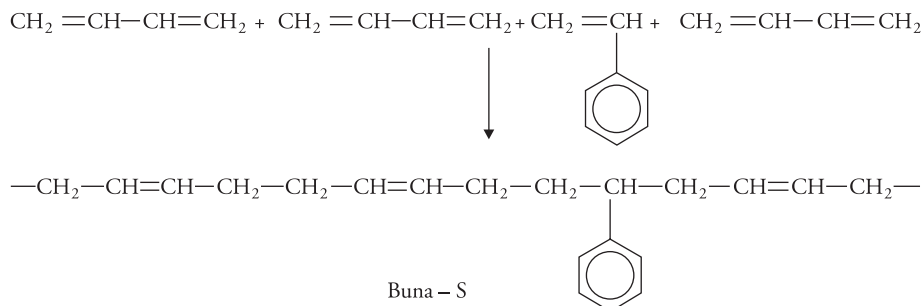
Table 6.2 Comparison of raw rubber and vulcanised rubber

Property	Non-vulcanised rubber	Vulcanised rubber
Tensile strength	70	700
Elongation at break %	1200	800
Permanent set	Large	Small
Rapidity of retraction (snap)	Good	Very good
Water absorption	Large	Small
Swelling in hydrocarbon solvents	Infinite (soluble)	Large, but limited
Tackiness	Marked	Slight
Useful temperature range	10 to 60 °C	−40 to + 100 °C
Chemical resistance	Poor	Much better

Synthetic rubbers**(i) Styrene butadiene rubber (SBR or Buna-S or GR-S)**

It is a random copolymer of butadiene and 10–25% styrene.

They are prepared by the copolymerisation of butadiene (75%) and styrene (25%) in an emulsion system at 50 °C in the presence of cumene hydroperoxide as a catalyst.



Vulcanisation of Buna-S is carried out by using either sulphur or sulphur monochloride (S_2Cl_2).

Properties

They are similar in many ways to natural rubbers and were the first widely used synthetics.

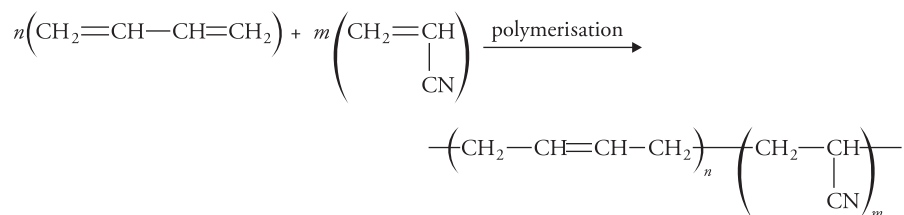
Like natural rubber, they are non-oil-resistant and are generally poor in chemical resistance. However, they have excellent impact and abrasion resistance. Carbon black is generally added as a filler to improve its abrasion resistance. They are oxidised easily and are below natural rubber in tensile strength and resilience.

Uses

Their single largest use is in the manufacture of motor tyres. They also find uses in the manufacture of footwear components, carpet backing, gaskets, adhesives, tank lining and insulation of wires and cable components.

Nitrile rubber (NBR or Buna-N or GR-A)

They are copolymers of butadiene and acrylonitrile.



Compounding and vulcanisation are similar to natural rubber.

Properties

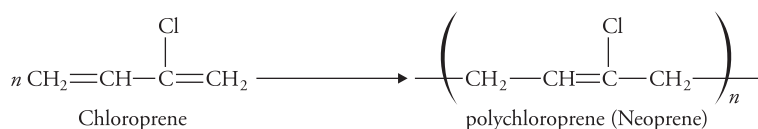
Nitrile rubbers are known for their outstanding resistance to oil and fuels both at normal and elevated temperatures. Nitrile rubbers are low in most mechanical properties. Their tensile strength is low and resilience is roughly one-third to half that of natural rubber. Their properties can be altered by varying the ratio of the two monomers. In general, as the acrylonitrile content increases oil resistance, tensile strength and processability improve, whereas resilience, low-temperature flexibility deteriorates. Elastomers with low acrylonitrile contents are used where good flexibility at low temperatures is required.

Uses

Nitrile rubber finds its use in the manufacture of flexible couplings, rubber rollers, printing blankets, washing machine parts, oil-resistant foams, hoses, adhesives, gaskets, lining of tanks, automobile parts and high-altitude aircraft components.

3. Neoprene (GR-M or polychloroprene) or polychlorobutadiene or duprene

It was developed in 1930s and has the distinction of being the first commercial synthetic rubber. It is prepared by the polymerisation of chloroprene, a chlorinated butadiene.



Properties

It is chemically and structurally similar to natural rubber. Its mechanical properties are also similar to natural rubber. Its resistance to oils, chemicals, sunlight, weathering, ageing and oxidation due to ozone are outstanding. It has excellent resistance to permeability by gases.

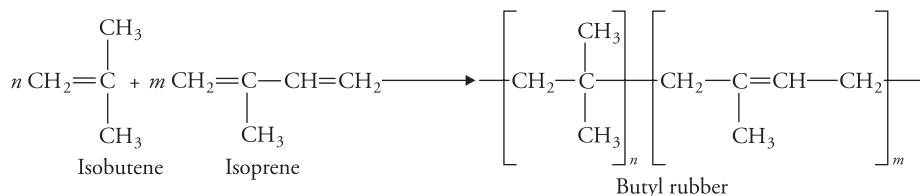
Its permeability is one-fourth to one-tenth the permeability of natural rubber depending on the gas. Being a polar polymer, its solubility in polar solvents is also higher. Although it is slightly inferior to natural rubber in most mechanical properties, neoprene has superior resistance to compression set, particularly at elevated temperatures. It retains its properties at temperatures upto 120 °C and is one of those few elastomers that does not support combustion, although it is consumed by fire.

Uses

It is used for making heavy duty conveyer belts, hose covers, footwears, brake diaphragms, motor mounts, tubing for carrying corrosive gases and oils, linings of reaction vessels and adhesives. Because of its low dielectric strength, it can be used for low-voltage insulation.

Butyl rubber (GR- I or Polyisobutylene-isoprene)

It is prepared by the aluminium chloride-initiated cationic copolymerisation of isobutylene and about 1–3% isoprene.



Properties

It is similar in many ways to natural rubber and is one of the lowest-priced synthetics. It possesses low gas and air permeability (about 10 times better than natural rubber).

Although they are non-resistant to oils, they have excellent resistance to sunlight, weathering, abrasion, tearing and generally have good chemical resistance. Because of its hydrocarbon nature, it is soluble in hydrocarbon solvents like benzene but is resistant to polar solvents like alcohol, acetone and ageing chemicals like HCl, HF, HNO₃, H₂SO₄, etc.

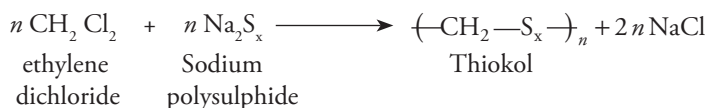
They also have good low-temperature flexibility (remains flexible upto -50 °C) and high heat resistance; however, they are not flame-resistant. They generally have lower mechanical properties such as tensile strength, resilience and compression set than the other elastomers. They can be vulcanised; however, due to low unsaturation they are not hardened much.

Uses

Because of its low permeability to gases it is used for making inner tubes of tyres, hoses, tubing and diaphragms. Because of their excellent dielectric strength, they are widely used for cable insulation and have a variety of electrical applications. They also find use in curtain wall gaskets, high-pressure steam hoses, machinery mounts, seals for food jars and medicine bottles, coated fabrics, etc.

Polysulfide rubber (Thiokol)

It is made by the reaction between sodium polysulphide (Na₂S_x) and ethylene dichloride:



Properties

Thiokol, a speciality polymer, is rated highest in having resistance to oil and gasoline. It also has excellent solvent resistance, extremely low gas permeability and is practically unaffected by ozone. Aging is very slow in this polymer. However, thiokol has poor mechanical properties like strength, compression set and resilience. It cannot be vulcanised and hence does not form hard rubber. Thiokol also has poor flame resistance and can be used only upto temperatures of 250 °F.

Uses

It is used in the manufacture of oil and gasoline hoses, gaskets, washers and diaphragms. It is widely used in liquid form in sealants for aircraft and marine industries. Moreover, in general, polysulphides form excellent fuel materials and become solid propellants for rockets when they are mixed with inorganic oxidizers such as ammonium perchlorate.

6.10 Fibres

Fibres are semicrystalline polymers that can be spun into long strands having length at least 100 times greater than their width or diameter. They have high strength-to-weight ratios and are used for textile as well as composite applications.

Classification

On the basis of their source, fibres can be (i) natural and (ii) synthetic.

Natural fibre It is a fibre made from a material originated from natural sources. Fibres can be derived from plants. For example, natural fibres can be cellulosic fibres (origin from plants like cotton, jute), protein fibres (origin from animals like wool, silk) or mineral fibres (from different rocks like asbestos fibre). Animal fibres are generally composed of keratin (fibrous protein found in skin, nails and hair), except silk filament, which is made up of fibroin.

Synthetic fibre The term synthetic fibre refers to materials that are developed by humans by using chemical and mechanical processes. Thus, synthetic fibres are commonly known as man-made fibres. Two types of synthetic fibres are commonly used in the textile industry: cellulosic and non-cellulosic.

Cellulosic fibres They are also known as regenerated fibres. They are derived from naturally occurring cellulosic sources such as wood pulp or cotton linters. The composition of these cellulosic fibres is altered by chemical reaction and polymerisation techniques to regenerate into a new form of fibre. For example, viscose rayon and cellulose acetate are regenerated from naturally occurring cellulose.

Non-cellulosics These are made totally by the man-made processes, by using chemical substances as the sources. Examples of these types are polyester, nylon, polyolefin and acrylics.

Fibres can also be classified from consumer's point of view into three types: (i) comfort fibres, (ii) safety fibres and (iii) industrial fibres.

Comfort fibres They are fibres that are used for making undergarments and garments, fibres used for making socks, underwears, ladies garments, shirting, suitings come in this category. These fibres should be soft and extensible and have adequate strength, flame retardancy and should be capable of being dyed. Examples of comfort fibres are cotton, silk, nylon, polyesters, acrylics, etc.

Safety fibres These fibres are used for making carpets, curtains, seat covers, etc. They should be tough, strong, durable and abrasion-resistant. These fibres should not burn easily, and should have minimum flame spread. If they catch fire they should liberate minimum heat, smoke and toxic gases. Examples are aromatic polyamides, polyimides, polybenzimidazoles and polyoxy diazoles are useful as safety fibres.

Industrial fibres These fibres have very high modulus, strength, thermal stability, toughness and durability. They are also called structural fibres and are used as reinforcing materials in composite structures. They are used to reinforce articles such as rigid and flexible tubes, pipes and tyres. Fibre-reinforced composites having high strength and stiffness on a weight basis are used in the construction of cars, planes, boats and even buildings. Uniaxially oriented fibres like aromatic polyamides, polyesters, carbon fibres and silica fibres belong to this category.

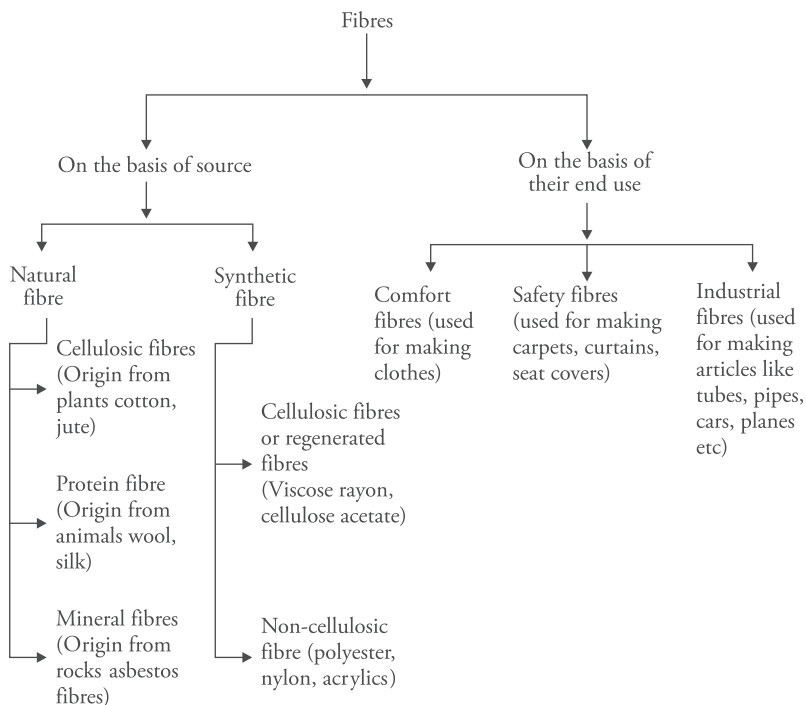


Figure 6.8 Classification of fibres

Fibre-spinning operations

The process of making fibres from polymers is called ‘spinning’. There are three principal spinning methods in use: (i) melt spinning, (ii) dry spinning and (iii) wet spinning.

Melt spinning includes spinning of a polymer in molten state. Polyamide, polyester and polyolefin fibres are generally obtained by the melt spinning process. In dry and wet spinning, the polymer is used as a solution in appropriate solvent. Solution spinning is used for cellulosic and acrylic fibres.

Melt Spinning

It was developed in the late 1930s. In this process the polymer is converted into a viscous mobile liquid by heating the polymer chips electrically and melting them in a heating grid. The molten polymer is surrounded by an inert atmosphere of N_2 , CO_2 or steam to prevent it from oxidative degradation due to environmental oxygen. The polymer is filtered using a filter pack (to remove lumps formed due to cross-linking or thermal degradation of the polymer during heating) and then it enters a metering pump, which pumps the polymer through a die having fine holes. This die is called the spinneret. Filaments emerging from the spinneret are cooled in a cold-air blast.

Cooled fibre is wound onto a spindle for subsequent treatment such as texturing and dyeing before being woven into fabric. The polymers that are generally melt-spun are polyolefins (for example, PE and polypropylene), polyamides (e.g., nylon 6 and nylon 6, 6) and polyesters.

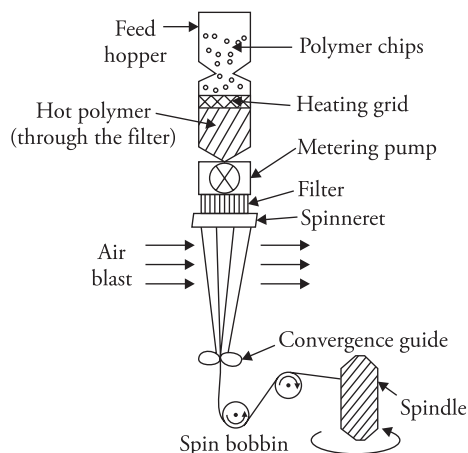


Figure 6.9 Schematic diagram of melt spinning

Dry Spinning

In this process, the polymer is dissolved in appropriate solvent in the range of 20–40%. The solution is filtered and pumped through a spinneret into a spinning cabinet (upto 25 feet in length). Dry nitrogen or heated air is passed from the lower end of the cabinet to enhance solvent evaporation. The dried fibre is then wound onto the spindle (bobbin). The fibres can be spun at a rate as high as 1000 m min^{-1} . Typical example of dry spinning is the manufacture of cellulose acetate fibres from a 35% solution of the polymer in acetone at 40°C . Other polymers that are converted into fibres using the above process are polyacrylonitrile and PVC.

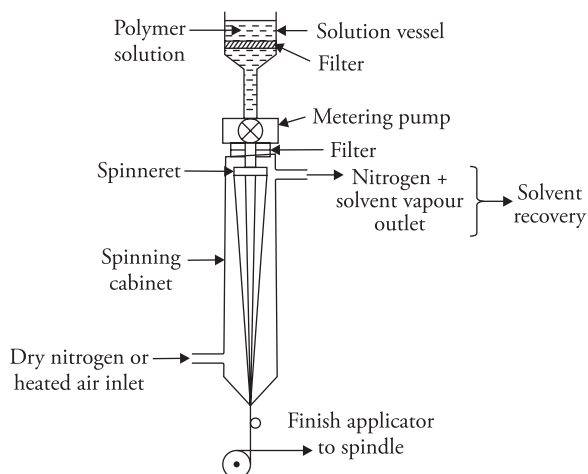


Figure 6.10 Schematic diagram of dry spinning

Wet spinning

It is one of the oldest fibre production methods. Wet spinning like dry spinning employs a fairly concentrated polymer solution. It differs from dry spinning in that the fibre is formed by the coagulation of the polymer solution by immersion in a non-solvent such as water. As shown in Figure 6.11, the spinneret is immersed into the non-solvent bath. The continuous jets of polymer coming out of the spinneret come in contact with a non-solvent and precipitate in the form of fine filaments. The filaments formed are washed, dried and gathered on a spindle.

The wet spinning process has been used to obtain fibres of polyvinylacetate (PVA), polyvinyl chloride (PVC), polyacrylonitrile (PAN), cellulose, viscose rayon, etc. PAN fibres can be wet-spun from dimethylformamide (DMF) solution into dimethylacetamide (DMAC) or from 50% sodium thiocyanate into aqueous 10% sodium thiocyanate. Similarly, polyurethane fibres such as spandex can be wet-spun from DMF solution into water.

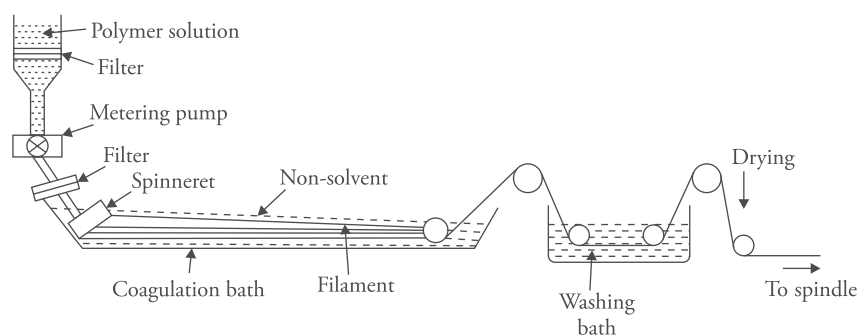


Figure 6.11 Schematic diagram of wet spinning process

Preparation, properties and uses of some important fibres

Cellulose acetate

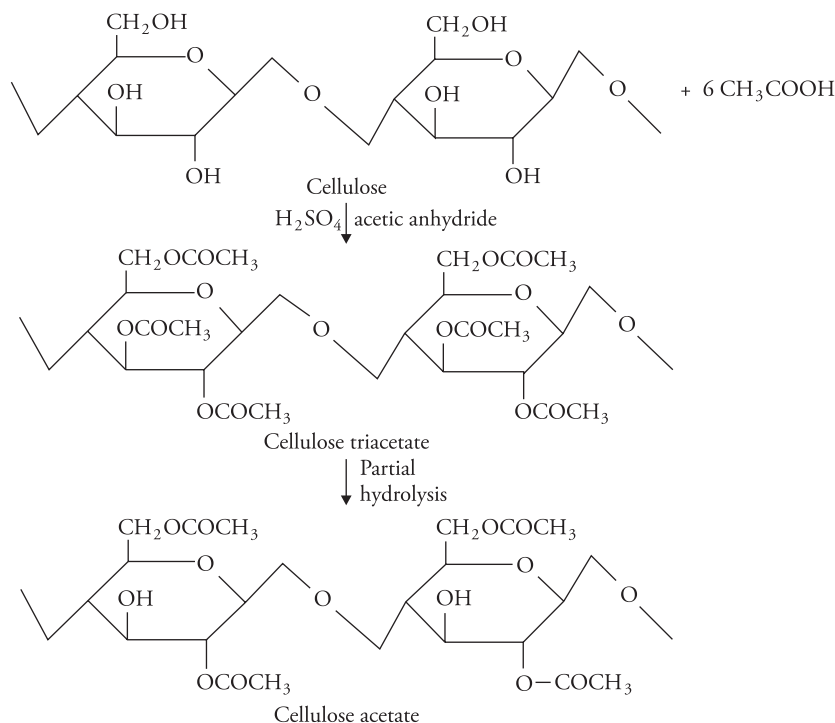
Preparation It was first prepared by Paul Schutzenberger of Germany in 1865. It is obtained by reacting cellulose obtained from processed wood pulp with acetic acid in the presence of acetic anhydride and traces of sulphuric acid in refluxing methylene chloride.

Cellulose triacetate is obtained. Commercial cellulose acetate is obtained by the partial hydrolysis of cellulose triacetate where the secondary acetate groups are hydrolysed.

Properties

Cellulose acetate is a white, amorphous product available commercially as powder or flakes. It is non-toxic, odorless, tasteless and a biodegradable polymer. It is lustrous, glossy, smooth, satiny with a silky finish, has high transparency, has good toughness and is skin-friendly. Its solubility, mechanical properties and compatibility with softeners, resins, varnish, etc depend on the degree

of esterification. It is hydrolysed by strong acids and alkalis, but resists the action of weak acids, animal and vegetable oils, gasoline, etc. It is sensitive to strong oxidising agents but is not affected by mild oxidising agents, peroxide solutions. The viscosity of the polymer depends upon the degree of polymerisation. Acetate fibres are stable against sunlight, relatively flame-resistant, have high melting point and have low conductivity, and hence serve as good insulating material.



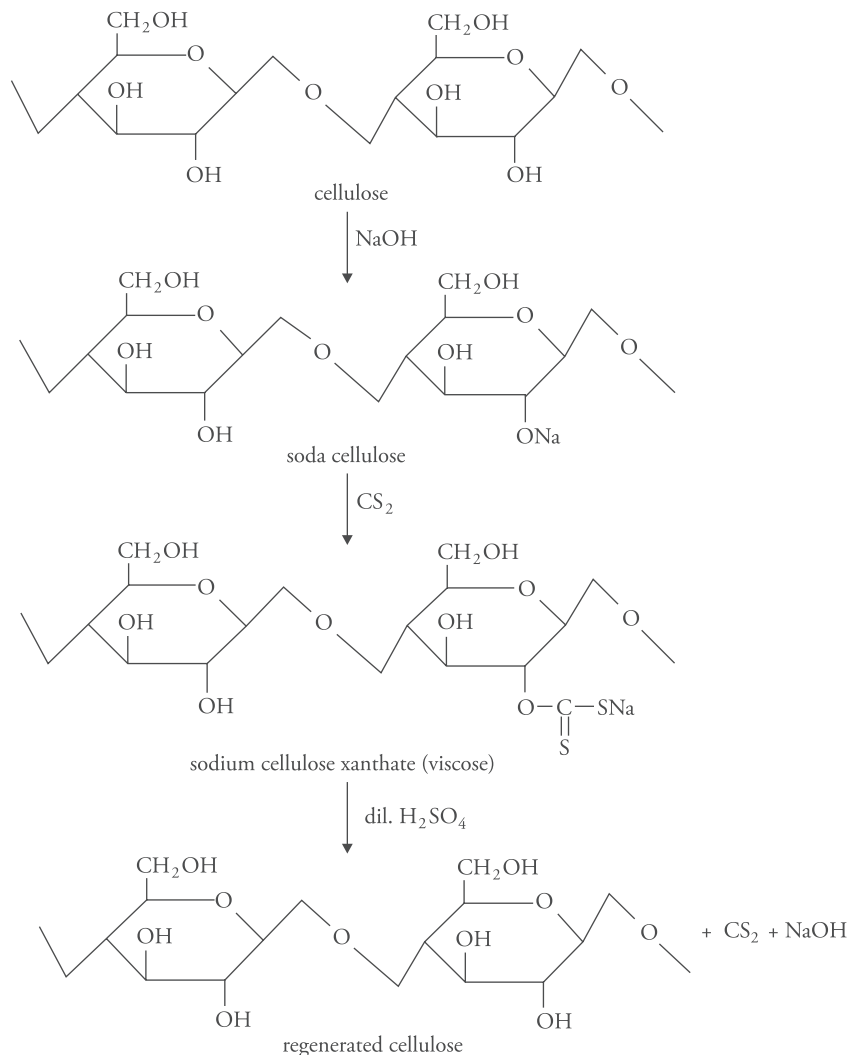
Uses

Cellulose acetate is used for making textile yarn. It cannot be dyed like viscose rayon. Acetate fibres are dyed with water-disperse dyes at the boiling point of the medium in the presence of carriers. The carriers enhance the dye uptake by the fibres.

Cellulose acetate also finds use in filter media including cigarette filters called 'tow'. Owing to their unique hydrophobic and hydrophilic properties, semipermeable membranes made out of these fibres are used in hemodialysis and desalination by reverse osmosis.

Blending these fibres with nylon or polyester makes them suitable for different end uses in linings, films, packing toys, playing cards, optical applications, frames of spectacles, eyeglasses, sporting goods, personal care products, etc. Being a biodegradable polymer, it also finds used in medical field. It is used for wound dressings and in the preparation of sustained release system for pills.

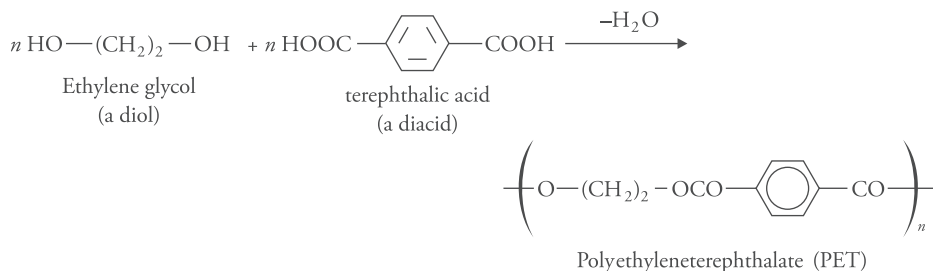
Viscose Rayon Viscose rayon is a fibre made from regenerated wood cellulose. Viscose rayon is prepared by treating either the pure cellulose or wood cellulose with 15–20% sodium hydroxide solution by which the cellulose is converted into soda or alkali cellulose. The alkali cellulose is then treated with carbon disulphide to form the alkali-soluble cellulose xanthate, which is allowed to stand for sometime. A viscous yellow liquid called *viscose* is formed, which is forced through the spinneret opening into dilute acid bath that regenerates the cellulose filament.



Polyesters

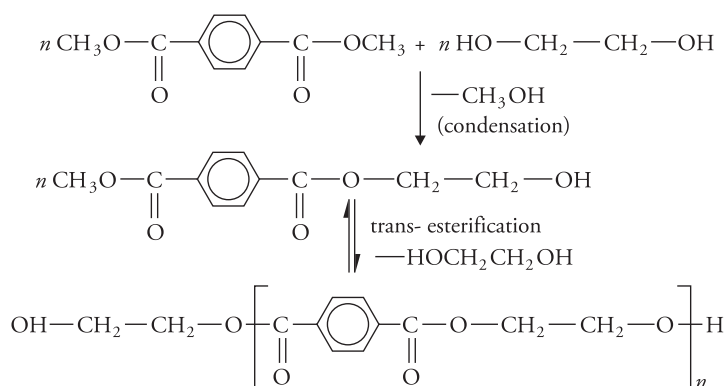
They are formed by the condensation of dicarboxylic acid with dihydroxyalcohol.

Polyethylene terephthalate (PET) a polyester is prepared by the condensation of terephthalic acid and ethylene glycol.



PET is commercially the most important polyester and is marketed under the trade name of *Terylene* or *Terene* or *Dacron*.

In commercial practice, dimethyl terephthalate (DMT) is used instead of terephthalic acid.



The first step (condensation) occurs at reflux temperature of ethylene glycol with a low vacuum. Methanol is recovered. The second step (trans-esterification) occurs at a high temperature of 200–250 °C under very high vacuum so that ethylene glycol is removed and the reaction proceeds in the forward direction.

Properties

PET (Terylene) is a very good fibre forming polymer. It is resistant to heat and moisture and melts at around 265 °C. It is inert to the attack of mineral and organic acids but is readily attacked by alkalis. PET fibres are oxidation-resistant, abrasion-resistant, have good mechanical strength upto 175 °C. They can also be dyed easily in the presence of a carrier.

Further, they are resistant to attacks by insects or moths.

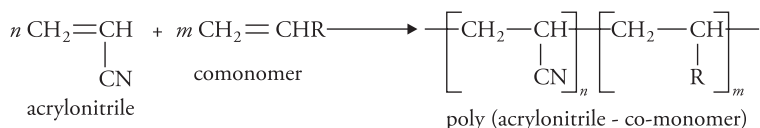
Uses

PET is used for making synthetic fibres like terylene, dacron. The garments made of these fibres are wrinkle resistant, have low moisture absorption and are not attacked by insects and moths. These fibres can be blended with wool and cotton to improve their properties. PET is also useful for making films that are used in the manufacture of magnetic recording tapes, transparencies for overhead projectors, etc.

They are used for electrical insulation due to their high dielectric strength. Glass-reinforced PET is used for the manufacture of toasters, car heaters, etc.

Acrylics

Acrylic fibre (or polyacrylonitrile fibre) is defined as a polymeric material that contains at least 85% by weight of acrylonitrile monomer. The comonomers are vinyl acetate and methyl acrylate. If the polymer contains large amounts of comonomers (from 15% to 50%) and at least 35 weight percent acrylonitrile monomer, then the polymer is considered as modified acrylic fibre and is referred to as modacrylic fibres.



Properties

Acrylic fibres have excellent chemical, biological, sunlight and weather resistance. They have high electrical resistance and good tenacity. They are resistant to moths, oils, chemicals but are attacked by strong bases. Acrylic fibres decompose before melting and hence cannot be made by melt spinning. Acrylic fibres are easy to wash and have good dimensional stability. They can be dyed in bright colors and the colors are very fast. They are lightweight, soft, warm and wool-like to touch.

Applications

Acrylic fibres are used for making apparels, sweaters, socks and tracksuits, sportswear, children's wear and as lining for boots and gloves. However, acrylics can cause irritation to people suffering from 'eczema'. They are used in furnishing fabrics, carpets, blankets, rugs upholstery, car tops, boat covers and outdoor furniture. Acrylics also find use in industries for making reinforcement materials in construction. Other industrial end uses include car batteries, filtration materials, etc.

Apart from acrylic fibres other acrylics in use are as follows:

Acrylic glass It is chemically polymethyl methacrylate PMMA or plexiglass.

Acrylic paints These are fast drying paints containing the pigment suspended in an acrylic polymer suspension. It is commonly used in modern fine arts. Acrylate polymers or resins are used to make hard plastics with various light-emitting properties.

6.11 Speciality Polymers

Engineering thermoplastics-Polycarbonate

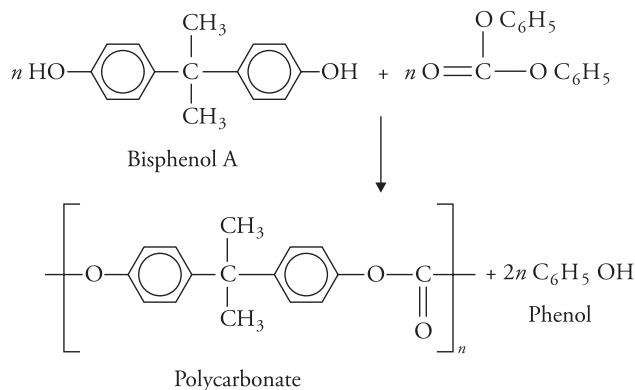
Polycarbonates are polyesters of phenols and carbonic acid. They can be prepared by the condensation of diphenoxymethylene derivatives with diphenyl carbonate.

2,2-bis(4-hydroxyphenyl) propane (bisphenol-A) on reaction with diphenyl carbonate gives polycarbonate.

Properties

Polycarbonate, a high-performance engineering thermoplastic, is a tough, strong, generally transparent, amorphous solid with outstanding impact resistance. It maintains its shape and size

even under great stress over a wide range of temperature. It is resistant to water, acids, detergents, oils and greases, but is attacked by bases, halogenated solvents (chloroform, carbon tetrachloride), ketones (acetones, acetonitrile), organic solvents like benzene, benzylalcohol, dimethyl ether, carbondisulphide, etc. It has excellent resistance to high temperatures upto 140 °C and maintains toughness at low temperatures upto -20 °C. It has good electrical insulation properties.



Uses

Owing to its electrical properties and dimensional stability, it is used for mouldings for computers, calculating machines, for making hair driers, electric razors, CDs and DVDs. Owing to its excellent impact resistance, it is used in automobile industry for making motorcycle windshields, police shields, headlight covers, car bumpers, front panels, safety helmets, etc.

As it is not stained by oils, greases and domestic beverages, it is used for making blenders, food processing bowls, coffee maker, food mixer housings.

Owing to its temperature resistance, stability and chemical inertness, it finds use in the manufacture of baby bottles, syringes.

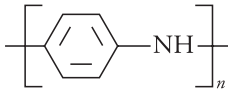

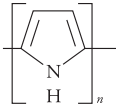

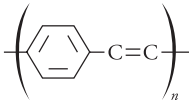
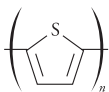
It is also used for making water dispensers, furniture (office and institutional), vacuum cleaner bases, cord hooks, impellers, spectacles, cameras and also for the manufacture of other unbreakable items.

Conducting Polymers

The use of polymers is increasing rapidly in our day to day life. Because of their light weight, corrosion resistance, easily workability, easy maintenance they are replacing metals in all walks of life. However, the drawback with polymers is that they do not conduct electricity. Research went on in this area and in 1977, three scientists Professor Alan-J. Heeger, Professor Alan. G Macdiarmid and Professor Hideki Shirakawa discovered that oxidation of polyacetylene with iodine results in 10^8 fold increase in its conductivity, that is, the conductivity of the doped polymer approaches the conductivity of one of the best conductors. The conductivity of doped 'polyacetylene' was found to be as high as 10^3 S cm^{-1} . This is comparable to the conductivity of copper on an equal weight basis. The three scientists received the Nobel prize in chemistry in the year 2000 for their discovery and the development of electrically conducting polymers.

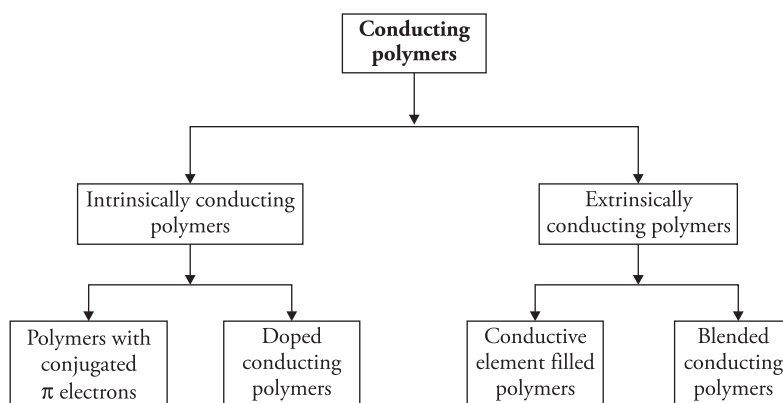
After the above discovery, research continued in this field and a large number of electrically conducting polymers were discovered gradually. Some common conducting polymers are as follows.

Table 6.3 Common conducting polymers and their conductivity

Conducting polymer	Repeating unit	Dopant	Conductivity (S cm^{-1})
Polyaniline		HCl	200
Trans polyacetylene		I_2 , Br_2 , Li, Na, AsF_5	10^4
Polypyrrole		BF_4^- , ClO_4^- , tosylate	500–7500
Poly(p-phenylene)		AsF_5 , Li, K	10^3
Poly(p-phenylene vinylene)		AsF_5	10^4
Polythiophene		BF_4^- , ClO_4^- , tosylate, FeCl_4^-	10^3

Classification of conducting polymers

Polymers that conduct electricity are called conducting polymers. They can be classified as follows.

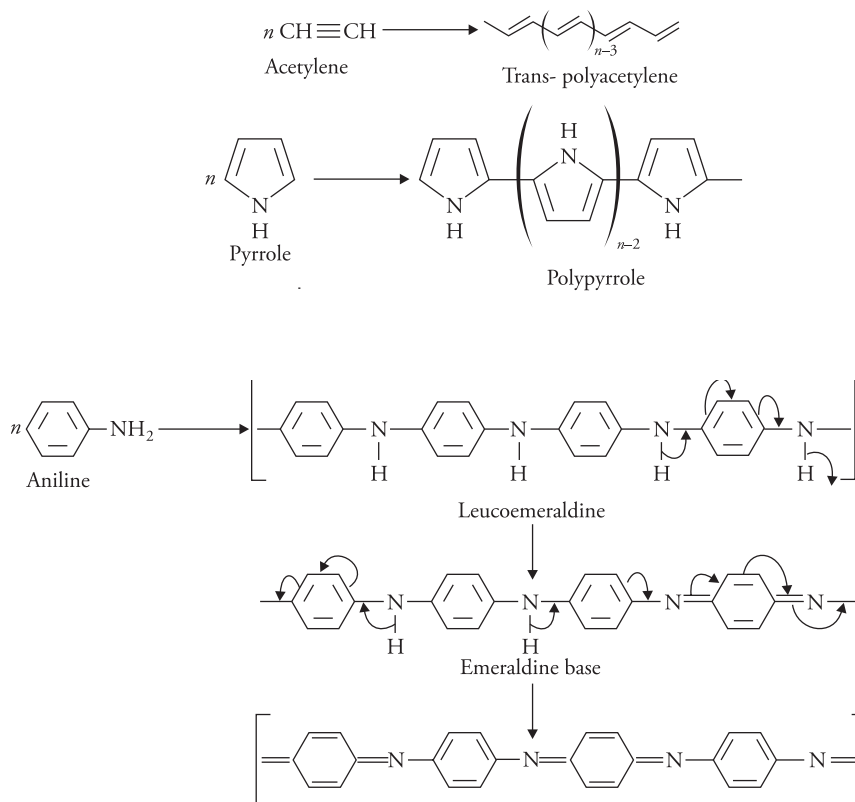
**Figure 6.12** Classification of conducting polymers

Intrinsically conducting polymers

The conductance of these polymers is due to the extensive conjugation in their backbone. They are further of two types.

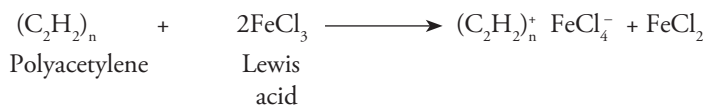
- (a) **Conjugated π -electron conducting polymers** The conductivity of these polymers is due to the presence of conjugated π -electrons. The conjugated π electrons are delocalised. In an electric field, the π electrons get excited and are transported through the solid polymeric material. However, the conductivity of these polymers is not sufficient for their use in various industrial applications.

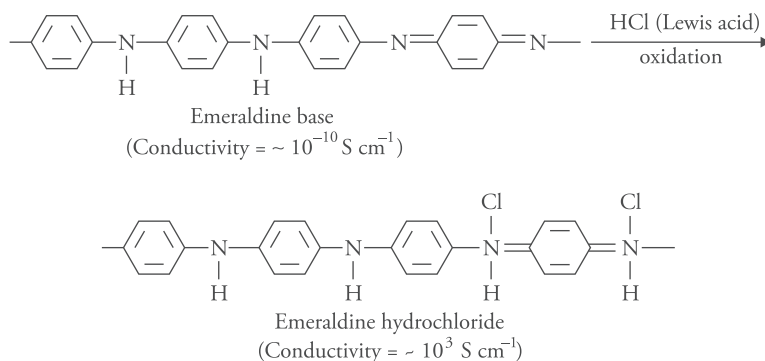
Example



All the three forms of aniline conduct electricity. The conductivity of polyacetylene is $1.7 \times 10^{-9} \text{ S cm}^{-1}$ and that of polyaniline is $10^{-10} \text{ S cm}^{-1}$. The conductivity is greatly enhanced by doping.

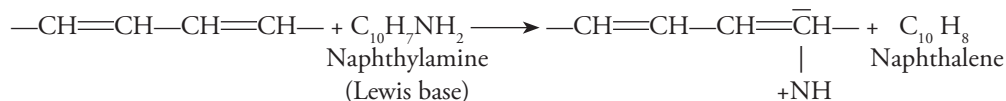
- (b) **Doped conducting polymers** The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types.
- (i) **p-type doping** When the polymer is treated with a lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p dopants are I_2 , FeCl_3 , Br_2 , AsF_5 , etc. For example,





Because of its conductivity it is also known as *synthetic metal*.

- (ii) **n-type doping** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, naphthylamine, etc. For example,



The conductivity of the above polymers depends on various factors.

- (i) **Length of conjugation of the polymeric chain** Greater the conjugation level, more will be the delocalised electrons and greater will be the conductivity.
- (ii) **Doping level** Conductivity increases with the increase in the amount of dopant.
- (iii) **Temperature** Contrary to metals, the conductivity of these polymers increases with the rise in temperature.

Extrinsically conducting polymers

The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

Conductive element-filled polymers When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises. Here the polymer acts as the binder of the conducting elements. However, addition of these elements affects tensile strength and impact strength of the polymer. This problem is overcome by blending a conventional polymer with a conducting polymer.

Blended conducting polymer Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties.

Applications of conducting polymers

Conducting polymers find use in electronics, solar cells, displays, illumination sources and microchips. Some of the major application areas are

- In rechargeable light weight batteries. These have perchlorate-doped polyacetylene-lithium system. These batteries are light in weight, leak-proof and small in size.
- Used in photovoltaic devices like in Al/polymer/Au photovoltaic cells.
- In telecommunication systems.
- Electrically conducting polyaniline is used for antistatic coatings, and also for producing 'smart windows'. Polyaniline shows different colors in different oxidation states. Hence, its color changes in response to sunlight or temperature changes.
- They are also used in organic light-emitting diodes (OLEDs).
- In electronic devices such as transistors and diodes.

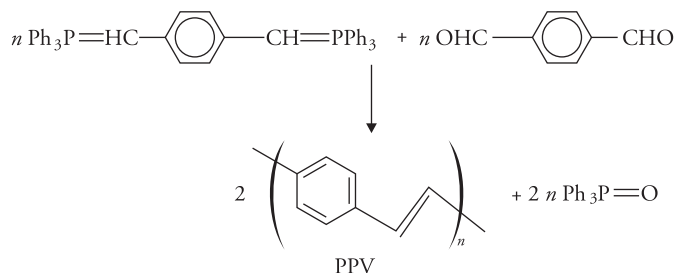
Electroluminescent Polymers

Electroluminescence is light emission stimulated by electric current. Electroluminescence in organic polymers has been known since early 1950s. Research continued and many organic polymers showing electroluminescence have been discovered. The phenomenon is particularly useful as enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels and optical amplifiers. A light-emitting diode (LED) is a crystalline semiconductor chip that glows. The first LEDs introduced in 1960s had only red and green colors. An OLED is made of sheets of polymer semiconductor material resembling plastic. Polymer LEDs were first discovered in 1989 by Richard Friend and co-workers at Cambridge University using polyphenylene vinylene (PPV) as the emissive layer.

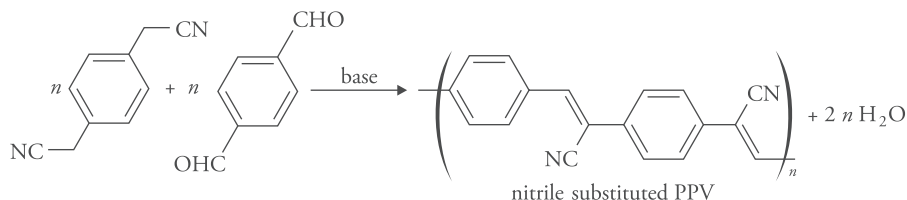
Polyphenylene vinylene It is the simplest and cheapest poly (arylenevinylene). It is the only polymer of this type that has so far been successfully processed into a highly ordered crystalline thin film.

Preparation

PPV can be synthesised by Witting-type coupling between bis (ylide) derived from an aromatic bisphosphonium salt and dialdehyde, especially 1, 4-benzenedialdehyde.



Knoevenagel condensation between a benzylic nitrile and an aromatic dialdehyde leads to the formation of PPV derivatives. Many side reactions occur in this method such as hydrolysis of nitrile group; hence, careful optimisation of the reaction conditions is needed.



Properties

- PPV is a bright yellow, fluorescent polymer. Its emission maxima is at 551 nm (2.25 eV) and 520 nm (2.4 eV). It lies in the yellow green region of the visible spectrum.
- It is insoluble, intractable and infusible. Incorporation of side groups like alkyl, alkoxy or phenyl increases the solubility of the polymer.
- It is a diamagnetic material with low intrinsic electrical conductivity (of the order of $10^{-13} \text{ S cm}^{-1}$). The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals or acids. However, the stability of these doped materials is low. Alkoxy-substituted PPVs are easier to oxidise than the parent PPV and hence have much higher conductivities.

Applications

Owing to its stability, processability, electrical and optical properties, PPV has been considered for a variety of uses. As PPV is capable of electroluminescence, it is used in polymer-based OLEDs. Devices based on PPV emit yellow green light. Derivatives obtained by substitution of PPV are used when light of a different color is desired. PPV is also used as an electron-donating material in organic solar cells.

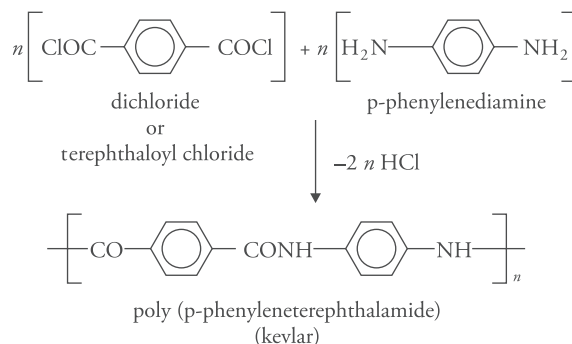
Limitations of PPV

It is susceptible to photodegradation and oxidative degradation in the presence of oxygen. Hence, precautions are to be taken to prevent oxygen contamination during manufacturing.

Liquid crystalline polymers

Liquid crystalline polymers are those polymers that are capable of forming regions of highly ordered structure while in liquid phase. The degree of order is somewhat less than that of a regular solid crystal. LCPs are very useful polymers because they have high mechanical strength at high temperatures. They also have extreme chemical resistance, inherent flame retardancy and good weatherability and are exceptionally inert.

A very commonly known liquid crystalline polymer is kevlar. It is an aromatic polyamide, poly(p-phenyleneterephthalamide). It is prepared by the polycondensation of aromatic dichloride and aromatic diamines.



Properties

Kevlar has extraordinary mechanical properties, high elastic modulus and high tensile strength. Kevlar is known for its ability to be spun into fibres that have five times the tensile strength of steel and 10 times that of Al on a weight to weight basis. The high tensile strength is due to extensive hydrogen bonding between the adjacent polymeric chains. It has extreme chemical inertness, high heat stability and flexibility. It is also extremely resistant to fire.

Uses

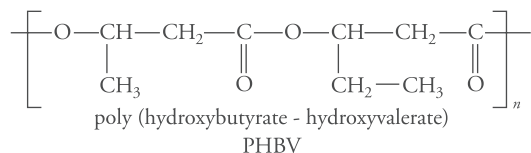
It is used in the fabrication of protective wear including bullet-proof vests. It is extensively used in aerospace and aircraft industries, boat hulls, drum heads, sports equipments, car parts (such as tyres, brakes, clutch linings), helmets, brake pads, ropes, cables, etc. LCPs are generally used as reinforced (composite) materials with carbon or glass fibres.

Presently, the high cost of liquid crystalline polymers limits its use to speciality applications like electronic components (e.g., computer memory modules), housings for light wave conductors and various aerospace applications.

Biodegradable polymers

Biodegradation is the degradation of a material by environmental factors such as sunlight, temperature changes or by the action of microbes (bacteria, fungi, etc.).

The use of biodegradable polymers is increasing day by day. Many natural polymers like rubber and cellulose are biodegradable. They degrade gradually by bacterial action. Biodegradable synthetic polymers are polyvinyl alcohol, hydroxyethylcellulose polymer, polycaprolactone, polylactic acid, hydroxybutyrate polymer, hydroxyvalerate polymer and poly(hydroxybutyrate hydroxyvalerate) (PHBV) a copolymer of hydroxybutyrate and hydroxyvalerate. PHBV is a biodegradable aliphatic polyester.



Applications

Biodegradable polymers find extensive use in the medical field. They are used commercially in tissue engineering and drug delivery field of biomedicine. Typical medical applications include the following.

- Use in orthopaedic fixation devices. Biodegradable polymers are used to join fractured bones. They provide the required strength to the bone and after the bone heals and can take the load, they harmlessly degrade over time. This prevents the patient from an additional operation for removal, as would be required if a metallic device was used.
- In controlled drug delivery, the polymer slowly degrades into smaller fragments releasing the drug gradually and in a controlled manner.
- It is used in dental devices, biodegradable vascular stents, biodegradable soft tissue anchors, etc. Biodegradable polymers are also being increasingly used in the manufacture of plastic bags, toys and other plastic products. These polymers gradually degrade in the environment (or in landfills) and leave the environment 'greener'.

6.12 Properties of Polymers

The properties of a polymer largely depend on their structural characteristics. Properties like tensile strength, elasticity, crystallinity, chemical reactivity and electrical properties depend upon various structural characteristics like chemical composition, sequence of monomer units, spatial arrangement of side groups, nature of packing, molecular weight, etc.

The various properties of polymers in light of their structural variations are discussed below

1. **Mechanical properties** Properties like strength, elasticity and hardness depend on the crystallinity of the polymer, whereas tensile strength and impact resistance are related to the molecular weight of the polymer.
 - (i) **Strength** Strength of a polymer depends upon the magnitude and distribution of intermolecular forces of attraction between the polymeric chains. Branched and straight chain polymers are held together by weak intermolecular forces of attraction. The magnitude of these forces increases with increase in length of the polymeric chain or the degree of polymerisation. Higher the degree of polymerisation greater is the strength of the polymer. Polymers with nearly 150–200 monomeric units show appreciable strength. Polymers with low molecular weights are soft and gummy. High molecular weight and long chain polymers are hard, tough and more heat-resistant.

Strength of a polymer can be controlled by making necessary changes in its structure. Polymers with polar groups like carboxyl, hydroxyl, chlorine, fluorine and nitrile are strong

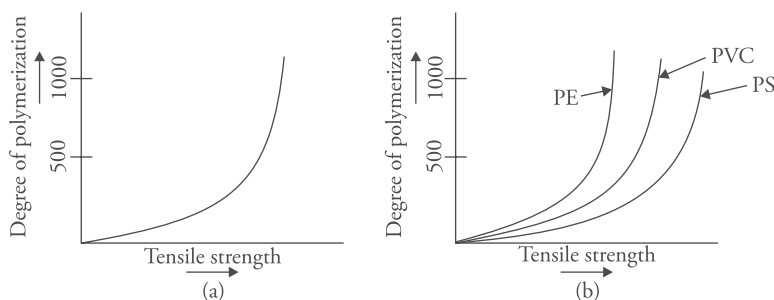


Figure 6.13 Dependence of strength of a polymer on degree of polymerisation

for example, nylon, polyester, etc. Nylon and terylene are strong due to the presence of hydrogen bonding between the polymeric chains. Similarly, teflon is the toughest known polymer because the fluorine atom is highly polar. Cross-linking also enhances the strength of the polymer. For example, natural rubber is soft. Introduction of sulphur cross-linkages (vulcanisation) greatly improves the strength of natural rubber.

Shape of a polymer also affects its strength. On comparing PE and PVC it is found that PVC is tougher. This is because the presence of chloride groups restricts the chain movement and increases van der Waals forces of attraction. Consequently, the chains cannot slip over each other and the strength of the polymer increases. Bakelite is a cross-linked polymer. All structural units are connected by strong covalent forces resulting in a giant solid three-dimensional molecule. Hence, they are strong and tough as the movement of chains is totally restricted.

2. Elastic deformation (elongation)

Elastic deformation or elasticity is the property by virtue of which a polymer changes shape under stress but recovers its original shape when the stress is released. The term 'elastomer' is generally used for such types of polymeric materials.

$$\text{Percentage elongation} = \frac{L}{L_0} \times 100$$

where

L_0 = original length of the polymer.

L = length of polymer after being stretched.

Elastomers can stretch from 500 to 1000 percent elongation and return to their original length without any difficulty. This is because unstretched polymer is randomly arranged (disordered with high entropy). On being stretched, the chains straighten resulting in crystallisation, entropy decreases; and so does the stability, and hence stiffening of the material takes place (Fig. 6.14). Hence, when the stretching force is released the chain returns to its original shape. A polymer behaves as an elastomer if it contains long chain of molecules having free rotating groups.

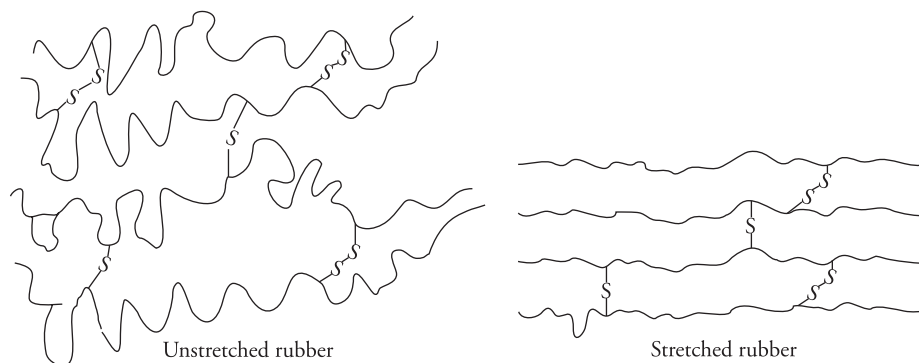


Figure 6.14 Effect of stretching on crystallinity of rubber

Rigid plastics such as polystyrene cannot be elongated. They break on applying excess stress. Flexible plastics like PE and polypropylene resist deformation to a large extent. Elastomers like rubber have high reversible elongation.

- (iii) **Plastic deformation** A substance is said to be in a plastic state if it is capable of flowing at some stage of its formation. Plastics are moulded into different shapes under flow condition. They retain their shape on cooling. Such materials that undergo plastic deformation on the application of heat and pressure are called thermoplastics. Generally, linear polymers whose polymeric chains are held together by weak van der Waals forces of attraction undergo plastic deformation very easily.

On the other hand, cross-linked polymers do not undergo plastic deformation. These polymers become hard and rigid due to the presence of primary covalent bonds throughout their structure. Owing to the presence of strong covalent bonds, the molecules cannot slip past each other; hence, plastic deformation cannot take place. These cross-linked polymers are called thermosets. If, however, their covalent bonds are broken by the application of heat and pressure, it results in total destruction of the molecule.

Solubility

The process of dissolution of polymers is very slow compared with simple molecules. First, the solvent diffuses into the polymer molecule producing a swollen gel. After that the solvent disintegrates the polymer leading to dissolution of the polymer.

The principle of 'like dissolves like' prevails for the polymeric molecules also. Non-polar polymers dissolve in non-polar solvents. Polymers with polar groups like $-\text{OH}$ and $-\text{COOH}$ are usually swollen or even dissolve in polar solvents like water, alcohol and ketones, but are resistant to chemicals like benzene, toluene, petrol and carbon tetrachloride. Polymers with aliphatic character are soluble in aliphatic solvents whereas those with aromatic character show greater solubility in aromatic solvents. Linear polymers dissolve because the solvent gets in between the chains. Cross-linked polymers only swell, they do not dissolve. Greater the cross-linking in the polymer, lesser is its solubility. Amorphous polymers containing bulky polar groups swell readily in polar solvents but do not form solutions at room temperatures. Crystalline polymers dissolve at high temperatures.

Chemical reactivity

The polymers like PE having all single bonds are mostly inert and undergo only substitution reactions. However, if the polymer is branched then oxidation may take place at tertiary carbon atoms. Polymers with double bonds are susceptible to oxidation. Polymers having ester, amide and carbonate groups are susceptible to hydrolysis. Polymers with free functional groups undergo reactions of those functional groups. For example, cellulose polymers with free hydroxyl groups react with nitric acid to produce nitrocellulose.

Electrical properties

Polymers are generally insulators, that is, poor conductors of heat and electricity. Electrical properties of a material are expressed as dielectric strength and dielectric constant. The **dielectric strength** of a material is defined as the maximum voltage which the material withstands and beyond which its dielectric nature is lost. The voltage is increased until the material breaks down; there is an arc across the electrodes and substantial current flows. It is expressed as voltage per unit thickness.

$$\text{Dielectric strength} = \text{V/mm or V/cm}$$

Dielectric strength helps us to evaluate the insulating properties of the material. Higher the resistance of a material for electric flow, larger is its dielectric strength or insulating capacity. Most plastics have good dielectric strength (in the order of 100–300 kV/cm). The other term which is used to determine the insulating or dielectric capacity of a material is the dielectric constant. Dielectric constant or permittivity ϵ is a dimensionless quantity and describes the ability of a dielectric to store electrically separated charges (electrostatic energy). It is defined as the ratio of the capacitance of a set of electrodes with the dielectric material between them to the capacitance of the same electrodes with vacuum between them. The dielectric constant for a vacuum is one and for all other materials is greater than one.

Electrical properties and polymeric structures

Dielectric properties of a polymer largely depend upon their chemical structure. The chemical structure determines whether a polymer is polar or non-polar and this in turn decides the electrical properties of the polymer.

In polar polymers like PMMA, PVC and nylon dipoles are created due to imbalance in the distribution of electrons. In the presence of electric field these dipoles tend to align with the field. This will create dipole polarisation of the material. Hence, these materials tend to be only moderately good as insulators. Their dielectric constant is high and generally lies between 3 and 7. Symmetrical molecular and non-polar polymers are truly covalent. No dipoles are present in these materials and the application of electric field does not align the dipoles. However, slight electron polarisation occurs due to movement of electrons in the direction of the electric field. This electron movement is instantaneous. Non-polar polymers like PTFE, PE, PP and PS have high resistivities and low dielectric constant. Their dielectric constant is always less than 3.

Table 6.4 Dielectric constant of some polymers

Polymer	Dielectric constant (1000 cycles)
Nylon 66	3.9 – 4.5
Cellulose acetate	3.4 – 7.0
PMMA	3.0 – 3.6
Polyvinylidene fluoride	7.46
Polybutene	2.25

Effect of environment on electric properties of polar polymers

Moisture and temperature of the environment have a considerable effect on the electrical properties of polymers. Polar plastics have a tendency to absorb moisture from the atmosphere. Presence of moisture raises the dielectric constant and lowers the resistivity.

If the temperature is raised, there is faster movement of the polymer chains and fast alignment of the dipoles. This holds good particularly if the temperature is raised above T_g , because above T_g , much more molecular movement is possible. Raising the temperature invariably raises the dielectric constant of polar plastics (i.e., lowers resistivity).

Non-polar plastics are not affected by water because they do not absorb water. Temperature does not affect electronic polarisation in non-polar plastics and hence does not have a marked effect on their electrical properties.

Crystallinity of polymers

The degree to which the molecules of a polymer are arranged in an ordered pattern with respect to each other is a measure of its crystallinity. Crystallinity has a vital role in determining the hardness, permeability, density, tensile strength, impact resistance, heat capacity and solubility of a polymer. In fact no polymer is 100% crystalline. Higher the crystallinity of the polymer, stronger is the secondary bonding and the polymer will be stronger and more brittle. Crystallinity of the polymer increases as the molecular weight increases. An isotactic polymer has higher crystallinity. Intramolecular bonding (e.g., hydrogen bonding in nylon and terylene) increases crystallinity.

Effect of polymer crystallinity on optical properties of the polymers

Amorphous polymers are generally transparent. They have a constant refractive index throughout the material. In crystalline polymers, the refractive index arising out of difference in densities of crystalline regions is different. There will be light scattering and the polymer will be translucent. Sometimes crystalline polymers are also transparent. If crystalline structures such as spherulites are smaller than the wavelength of light, they will not interfere with the passage of light. As a result, the polymer will appear transparent.

Effect of polymer crystallinity on permeability

Permeability is defined as the rate of penetration of liquid or gases through the polymer matrix. It depends on polymer crystallinity. Crystalline polymers have close packing and hence permeability is quite low. Amorphous polymers above glass transition temperature have enough free volume between the molecules. Hence, liquids and gases pass through them making them permeable.

Thermal behavior of polymers

Glass transition temperature (T_g) is defined as the temperature below which an amorphous polymer (sometimes crystalline polymer) becomes hard, brittle and breaks like glass. Above this temperature it is soft, flexible and rubbery. The hard and the brittle state is called the glassy state because random arrangement of polymeric chains is similar to the random molecular arrangement found in glass. The soft, flexible state is the rubbery or *viscoelastic state*. On heating beyond T_g the polymer first changes into soft, flexible rubbery state and then converts into the highly viscous liquid and starts flowing. This is called as viscofluid state and the temperature at which this occurs is called the flow temperature T_f as explained in Figure 6.15.

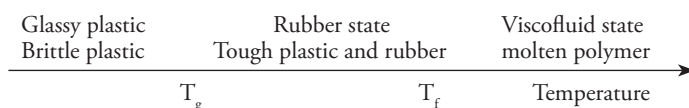


Figure 6.15 Thermal behavior of Polymers

Some polymers are used to above T_g and some below. Hard plastics like polystyrene and polymethylmethacrylate are used below T_g , that is, in their glassy state. Rubbers, elastomers like polyisoprene and polyisobutylene are used above their T_g , that is, in their rubbery state when

they are flexible. Some polymers like polycarbonate, although amorphous, are considered tough at temperatures well below their T_g . This behavior is because of the chemical bonds in polycarbonates rather than the arrangement of the polymeric chains.

The above phenomenon can be explained considering the three states of matter solid, liquid and gas. Polymers however exist only in two phases solid and liquid because they decompose before reaching their boiling points. In a long chain of polymer molecule, some segments have freedom of movement while others do not. When such a polymer molecule is heated first there is internal mobility of the polymeric segments (called segmental mobility), and then the whole molecule starts moving (molecular mobility; segmental mobility can be compared with the audience standing in their position or stretching their arms while watching a movie, whereas molecular mobility is the moving out of the audience during intermission or after the movie). When segmental mobility comes into play the solid polymer acquires a soft and rubbery state. With the onset of molecular mobility the polymer changes into the liquid state.

Behavior of amorphous polymer In an amorphous polymer, there is absence of long range order in the solid state. When such a solid is heated the energy increases. The segmental mobility increases followed by increase in molecular mobility; hence, it changes into liquid form. During the transition of an amorphous solid into liquid there is no change in the internal order of the molecular arrangement (molecules are randomly arranged both in solid and liquid states), there is change only in the energy of motion. If such a liquid is cooled the absence of long-range order, which is a characteristic of liquid phase, is retained. However, because of decrease in thermal energy the molecule loses its ability to move and becomes immobile or becomes solid physically. Hence, a glassy solid is considered as a super-cooled liquid. At low temperature, an amorphous polymer does not possess segmental or molecular mobility and exists as glassy solid. On heating gradually, it acquires segmental mobility and becomes rubbery. The temperature at which the amorphous polymer passes from glassy state to rubbery state is called the glass transition temperature T_g . On further heating, molecular mobility sets in and the polymer passes into liquid state and starts flowing; this is the flow point temperature T_f .

Behavior of crystalline polymer

A crystalline polymer has long range order. All the atoms or molecules of the polymer occupy fixed position in the crystal. The segments in crystalline polymer are held by strong intermolecular forces; hence they do not possess segmental mobility. The energy required to overcome these intermolecular forces is almost equal to the energy required to induce molecular mobility. Hence, when a crystalline polymer is heated segmental mobility alone cannot set in and hence the polymer does not pass into rubbery state and does not possess a glass transition temperature. It changes directly into liquid state. The temperature at which a crystalline polymer changes into liquid state is called the melting temperature T_m .

Behavior of semicrystalline polymer

Polymers are mostly partially crystalline and consist of both amorphous as well as crystalline regions. Such polymers have both glass transition temperature T_g as well as melting temperature T_m . Below T_g the amorphous region exists in glassy state and the crystalline region is in crystalline state. At T_g the amorphous region passes into rubbery state, whereas the crystalline region remains crystalline. At T_m crystalline region melts into a liquid state. Beyond T_m the amorphous and crystalline regions become one and the polymer as a whole is in liquid state.

Factors effecting T_g

1. **Molecular weight** As the molecular weight increases, bulkiness increases and hence T_g increases.
2. **Molecular structure**
 - (a) Insertion of bulky inflexible side group increases T_g because of decrease in mobility.
 - (b) Increase in the length of the side chain, presence of double bond in the backbone of polymeric chain decreases T_g .
 - (c) Increase in cross-linking decreases mobility and increases T_g .
3. **Plasticiser** Addition of plasticiser to the polymer helps the polymeric chains to slide past each other even at low temperature resulting in decrease in T_g .
4. **Water or moisture content** Increase in moisture leads to increase in the formation of hydrogen bond with polymeric chain. This increases the distance between the polymeric chains. The increase in free volume between polymeric chains results in the decrease in T_g .
5. **Cooling rate** If the cooling rate of molten solid is higher, the T_g is higher. Moreover, if the rate of cooling is slower, then T_g obtained is low.
6. **Flexibility of polymer chain** Polymers in which the polymeric chains are flexible have low T_g , whereas those in which the chains do not move have high T_g .
7. **Branching** Increased branching results in decreased mobility of the polymer chain and increased chain rigidity results in high T_g .

Importance of T_g

The T_g value gives information whether the polymer could be used as rubber or plastic. The materials having low T_g are usually sticky in nature. Hence if the T_g of the material is increased by addition of substance having high T_g values then the product would not be sticky. It becomes hard and easy to process for industrial use. In glassy state, the substance is tough and has good strength. Glass transition temperature can be used to modify physical properties of solids. By altering T_g of the polymer or drug they can be maintained in an amorphous solid form at ambient or body temperature. Improvement in handling characteristics, solubility and reproducibility in dissolution of solids can be achieved by increasing the T_g of solids.

Anelasticity

Elastic deformation is **time-independent**, that is, an applied stress produces instantaneous elastic strain that remains constant over a period of time till the stress is maintained. Upon release of the stress, the strain is totally recovered and the material returns to its original undisturbed position.

In most engineering materials, there exists a **time-dependent** elastic strain component. In this, the elastic deformation continues after the application of stress and the material takes a finite time for the recovery after the release of stress. This time-dependent elastic behavior is called **anelasticity**. This effect is also termed as **elastic after effect**.

In some materials, when they are loaded, the material undergoes a certain instantaneous elastic deformation E_{el} , followed by a delayed or retarded elastic deformation E_{an} (anelastic effect) during a time t , which approaches a final value asymptotically. If the load is removed, the instantaneous elastic recovery, equal to E_{el} is followed by a delayed recovery in time t .

For metals, the anelastic component is generally small and often neglected. However, for polymeric materials its magnitude is significant. In this case, it is termed as **viscoelastic behavior**.

Viscoelasticity

There are two types of deformations (or strains): (i) elastic deformation and (ii) plastic deformation.

- (i) **Elastic deformation** is reversible. When stress is applied, the atoms in a material move and come back to their original position on the removal of stress. A rubber band is a typical example of this type. It stretches on applying force and returns to normal condition when the stretching force is removed.
- (ii) **Plastic deformation** is a permanent deformation. When the stresses are released, the atoms do not return to their original states and consequently the material remains deformed. The deformation or load remaining after load release is referred to as the **permanent set**.

A third kind of deformation called **viscoelasticity** is found in some polymers, such as plastics. Here, when the applied stress, which is within the materials' elastic range, is removed the material will not completely recover its original size. If a force is applied on a polymer and withdrawn quickly, the polymer tends to return to its original undisturbed configuration, a process called relaxation (elastic behavior). If the force is applied gradually and consistently, the molecules begin to flow irreversibly. The flowing liquid will be viscous because of chain entanglement and frictional effects. This combination of properties *elasticity* and *viscous flow* is referred to as **viscoelastic behavior**. This behavior is ideally illustrated by Silly Putty, a siloxane polymer. If rolled into a ball and dropped to the floor, it will bounce back demonstrating its elastic behavior. However, if strain is applied gradually the ball will elongate with high extension (viscoelastic behavior). If left on a desk for several days, the ball will flatten and flow like a viscous liquid over long time.

Viscoelastic behavior is dependent both on time and temperature. This behavior has been quantified experimentally. In these tests, a specimen is initially strained rapidly in tension to a predetermined and relatively low strain level. Keeping temperature constant, the stress necessary to maintain this strain is measured as a function of time. Stress is found to decrease with time because of molecular relaxation process taking place within the polymer.

Relaxation modulus $E_r(t)$, a time-dependent elastic modulus for viscoelastic polymers, may be defined as

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_0}$$

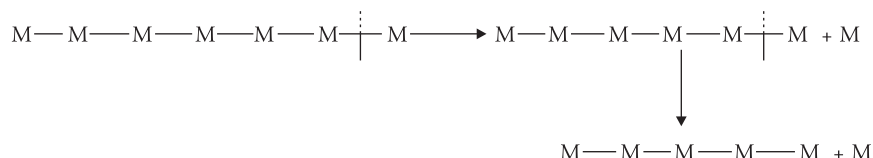
where $\sigma(t)$ is the measured time-dependent stress and ε_0 is the strain level that is maintained constant. Moreover, relaxation modulus is a function of temperature, and to fully characterise the viscoelastic behavior of a polymer isothermal stress relaxation measurements must be conducted over different temperature ranges.

As most polymers exhibit both anelastic and viscous responses to external forces, models for such viscoelastic behavior consist of viscous and elastic elements. The spring illustrates purely elastic behavior and the dashpot purely viscous behavior.

Mechanical stress, radiation, oxygen and other environmental factors are generally responsible for the degradation of a polymer. Polymers also degrade during fabrication process when they are subjected to high temperatures.

Types of polymer degradation

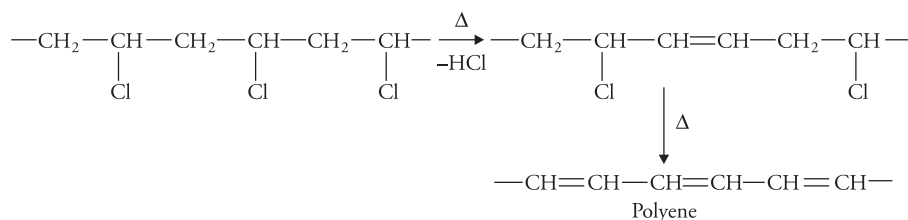
(i) **Chain end degradation** In this type, the degradation starts from the chain end releasing the monomeric units. This phenomenon is the reverse of chain propagation and is also termed as 'depolymerisation'.



- $$\text{M}-\text{M}-\text{M}-\text{M}-\text{M}-\text{M} \longrightarrow \text{M}-\text{M}-\text{M}-\text{M}-\text{M} + \text{M}-\text{M}$$

Factors responsible for degradation

- (a) **Thermal degradation** Degradation under the influence of heat is termed as thermal degradation. Thermal degradation occurs by both chain end degradation, leading to the formation of monomer units, or by random degradation. Besides the above two types of degradation, non-chain scissions also occur, which involve the pendant (substituent) groups without affecting the main chain. For example, PVC degrades at about 200 °C releasing HCl. As a result of this degradation, the color of PVC changes from white to black.



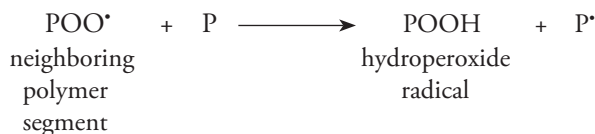
- (b) **Degradation by radiation** It is brought about by ultraviolet or visible light. Also called photodegradation, it is responsible for the yellowing and gradual embrittlement of plastic material on storage. Ultraviolet or visible light causes 1,1-disubstituted polymers to degrade to monomers almost exclusively at room temperatures. Polymethylmethacrylate gives a quantitative yield of the monomer in the presence of ultraviolet rays. Generally, photostabilisers like 'salol' are added to protect the polymers from deteriorating in the presence of light.
- (c) **Oxidative degradation** It leads to the hardening, discoloration and surface changes in the polymer. Saturated polymers degrade very slowly by oxygen, whereas unsaturated polymers are easily attacked by oxygen. It is believed that oxidative degradation proceeds by the formation of hydroperoxide radical, which is mainly responsible for chain incision.



P- represents the polymer chain.



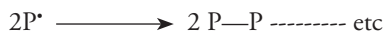
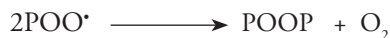
POO[•] abstracts hydrogen from the neighbouring polymer chain P and forms hydroperoxide radical.



The hydroperoxide leads to the formation of several new free radical sites.



The recombination of free radicals occurs leading to chain termination.



- (d) **Mechanical degradation** Some polymers degrade under mechanical stress. Polystyrene dissolved in a solvent when stirred vigorously undergoes molecular degradation or fragmentation. Similarly, rubber on being subjected to mechanical stress called mastication undergoes chain scission, leading to the formation of low-molecular-weight fragments.

Polymers also undergo degradation by ultrasonic waves, X-rays, gamma rays, alpha rays, beta rays and other high-energy radiations.

6.14 Polymer Composites

A composite material is a hybrid material formed by the combination of two or more dissimilar materials to produce a new material, having the advantageous properties of the different components. A composite material is better suited for a particular application than either of the original materials alone.

Modern technologies require materials of unusual combination of properties that cannot be met by the conventional polymeric materials, alloys, ceramics and cements. These materials can be combined in composite material to produce unique characteristics such as stiffness, toughness, high temperature strength. These types of materials find use particularly in aerospace, underwater and transportation applications. The composite materials comprise of two phases 'matrix', which is the continuous phase and the 'dispersed phase' or the reinforcing material.

The most common example of a composite material is the fibre-glass reinforced plastic. The plastic acts as the matrix and fibre glass is the dispersed phase. Plastic alone is relatively weak and has a low elastic modulus, that is, it bends and stretches easily. The glass fibres provide it strength and stiffness, and their modulus of elasticity may be 50 times greater than that of plastic alone. Glass fibres take most of the load when the composite is stressed.

Fibre-reinforced plastic (FRP) They are composites that contain fibre in the dispersed phase. The design goals of fibre reinforced composites often include high-strength and stiffness on a weight basis.

Glass-reinforced plastics (GRP) Glass-reinforced plastic is popularly known as 'fibreglass'. It is a composite material made of plastic material reinforced by fine glass fibres in the dispersed phase.

Properties

Dimensional stability Glass fibre exhibits dimensional stability. It does not stretch or shrink on exposure to extremely high or low temperatures.

Moisture resistance Glass fibres do not absorb moisture.

High strength They have high strength-to-weight ratio. This property makes them useful for applications in areas where high strength and minimum weight is required.

Fire resistance Being inorganic in nature, glass fibre does not burn or support combustion.

Chemical resistance They are chemically inert. However, they are affected by hydrofluoric acid, hot phosphoric acids and strong alkaline substances.

Electrical properties They have low dielectric constant. Glass fibres are excellent materials for electrical insulation.

Uses

The combination of properties such as low moisture absorption, high strength, heat resistance, chemical inertness and low dielectric constant makes glass fibres ideal polymers for a variety of end uses. They are mainly used in the aerospace industry for making high-performance aircraft (gliders), boats, automobiles, hot tubs, water tanks, baths, pipes, etc. They are used for making mats and fabrics for thermal insulation, electrical insulation, sound insulation, high-strength fabrics, heat- and corrosion-resistant fabrics. They are also used to reinforce various materials like translucent roofing panels and automobile bodies. GRP pipe systems are used over and under the ground for firewater system, drinking water system, gas system, waste water or sewage system.

GRPs are also used in construction of buildings and for producing chimneys. GRPs can be used to construct panels with appropriate insulation, which reduces heat loss.

Owing to their light weight characteristics, they are used for making helmets, sports use articles like goal tender masks or catches masks. Fibre glass also finds use in the telecommunication industry.

Manufacture methods The various techniques employed for the manufacture of reinforced plastics are

- (a) Hand lay-up technique
- (b) Filament winding technique
- (c) Spray lay-up technique
- (d) Pultrusion

(a) Hand lay-up technique

In this process, the mould used is coated with a thin coating of polyvinyl alcohol, silicone oil or wax to prevent the polymer from sticking to the mould. The resin matrix or plastic matrix is then put in the mould followed by glass mat or cloth. Then another layer of resin is put. These layers are then pressed with the help of rollers. Alternate layers of glass, cloth and resin are laid until the required thickness is built. The whole set up is then cured at ambient or elevated temperature. The reinforced plastic is then removed from the mould. It is finally trimmed and finished. This technique is used to produce auto body parts, boat hulls, ducts and building components.

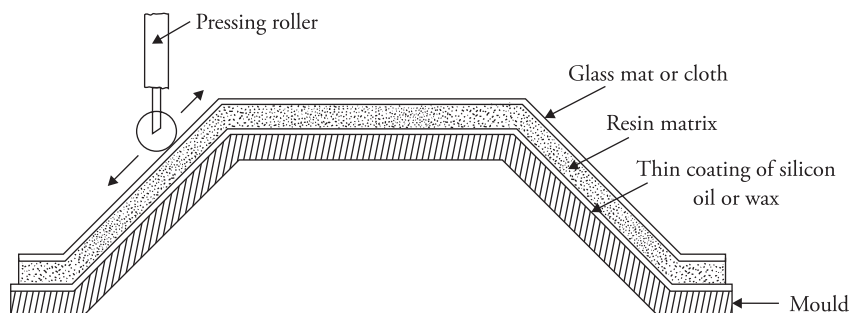


Figure 6.16 Schematic diagram of hand lay-up technique

(b) Filament winding technique

In this process, fibres are pulled from spindles and passed through a bath containing composite resin such as epoxy resin. The excess resin is squeezed out of the strand coming out of the resin

bath. The resin-dipped filament is wound onto a mandrel in some predetermined manner. Once the mandrel is uniformly covered to the desired thickness and fibre orientation, the composite is cured at an elevated temperature. The mandrel may be removed later or left as an integral part of the composite.

Filament winding is used for producing reinforced plastic articles such as corrosion-resistant (fibre glass) tanks, pipes and high-pressure cylinders. It is used to prepare composites for use in aerospace and automotive industry.

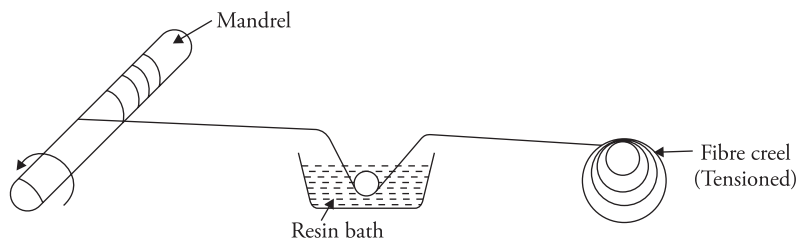


Figure 6.17 Schematic diagram of filament winding technique

(c) Spray lay up technique

In this technique, the resin, a curative, and the chopped fibres are sprayed simultaneously in a combined stream from a spray gun onto a mould. Once the desired thickness is achieved, it is compacted and then cured, cooled and removed from the reusable mould. Before application of fibre and resin, the mould is prepared with either polyvinylalcohol or non-silicon wax to facilitate the release of the product. This technique is used to produce reinforced plastic articles such as truck bodies, storage vessels, boat hulls, lorry, cabs, etc.

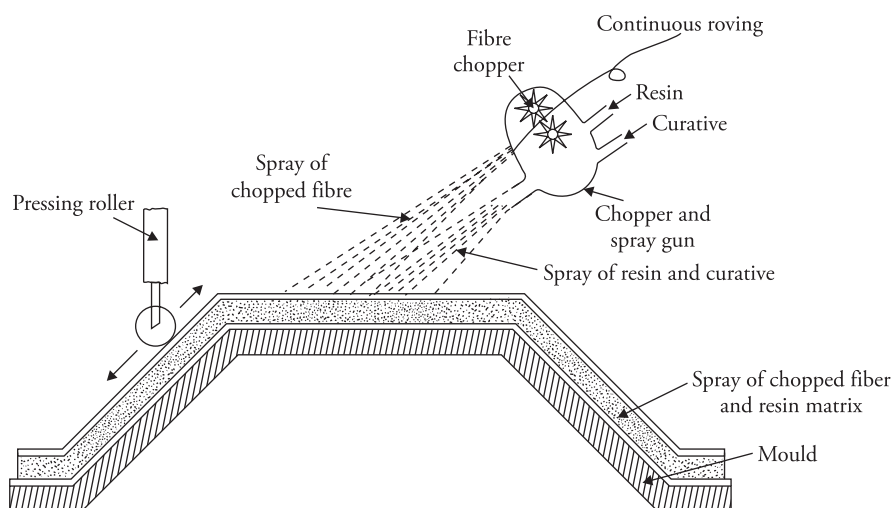


Figure 6.18 Schematic diagram of spray lay up technique

(d) Pultrusion

Pultrusion is the process for manufacture of composite materials with constant cross-section. It involves 'pulling' of raw material through a shaped die. The term pultrusion combines the words, 'pull' and 'extrusion'.

The pultrusion process starts with racks or creels holding rolls of fibre. This raw fibre is pulled off the racks and is guided through the resin bath. In some pultrusion systems, the resin is injected directly into the die.

The fibre becomes impregnated with the resin. The resin-impregnated fibre passes through the 'preformer' where the excess resin is squeezed out. The composite now passes through a heated steel die where the resin undergoes polymerisation. Initially, the die used was stationary but these days moving dies are also used. The cured pultruded fibre-reinforced polymer (FRP) composite then passes through the rollers. At the end of the pultruded machine is a cut off saw that cuts the fibres into specific length.

This technique is used for the manufacture of fibres used in agriculture, chemical industry, sports, etc.

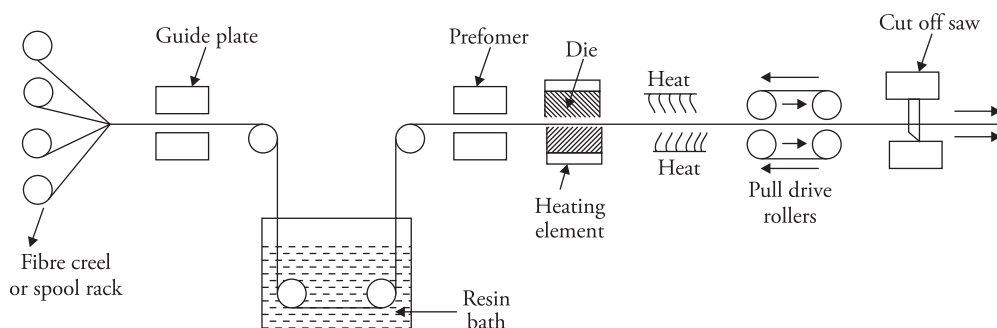


Figure 6.19 Schematic diagram of pultrusion technique

6.15 Adhesives

An adhesive is a substance, organic or inorganic, natural or synthetic, that is capable of bonding two or more substances together by surface attachment.

Adhesives are generally applied as a thin film between the surfaces to be joined, in either a plastic or liquid state and it gradually hardens due to the evaporation of the solvent, adhering the two surfaces together.

Adhesive is a general term and it includes cement, gum, glue, fevicol and paste.

Classification of Adhesives

Adhesives can be classified in various ways. A brief description of some important classes of adhesives based on their chemical nature is given as follows.

1. Natural resin adhesives

- (a) **Vegetable glues or protein glues** They are prepared from soyabeans and corn. These include starch, gum, etc. They are used for common adhesive jobs like bonding paper.
- (b) **Animal glues** They are popular variety of protein glues that can be prepared from bones of dead animals, wastes of animals, fish, hide scrapes from leather industry, casein and blood albumin. These are used in furniture, radio cabinets, etc. Shellac resin obtained from an insect is one of the oldest adhesive. It possesses good strength and is to be applied when hot.
- (c) **Natural adhesive** Like asphalt, it is used for bonding paper, cloth and also for metal bonding.

2. Synthetic adhesives

(I) Thermoplastic resins

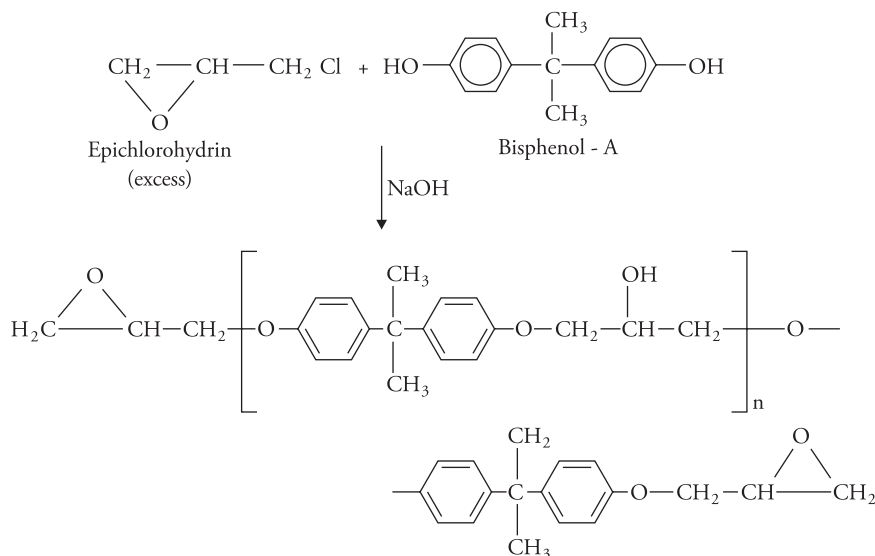
- (a) **Cellulose derivatives** Cellulose acetate and cellulose nitrate when mixed with benzene and alcohol, respectively, show excellent bonding properties.
- (b) **Acrylics** Like plexiglass (PMMA), they are used for bonding cloth, glass, paper, etc.
- (c) **Polyvinyls** Like PVA and PVC, they are also good adhesives.

(II) Thermosetting plastic resins

- (a) **Phenol formaldehyde resins** These are used for making water-proof plywood, laminates and for bonding articles in spacecraft and shipbuilding industries. The resin is applied between the two surfaces and then cured by heating and pressing.
- (b) **Urea formaldehyde resin** They are syrupy, transparent compound generally used as such or after mixing with water. End uses are similar to phenol formaldehyde resin.
- (c) **Polyesters** They work as good adhesives on being mixed with alkyd resins. They are employed for making laminated glass and cloth.
- (d) **Silicone resins** They are stable, water repellent used for bonding metals, ceramics, plastics, rubbers, etc.
- (e) **Epoxy resins** They have very good adhesion properties. They can be used in solid as well as liquid forms. The solvent evaporates leaving behind a very thin film that provides excellent adhesion. Araldite is a very good example of epoxy resin.

Preparation of epoxy resins

They are prepared from epichlorohydrin and bisphenol-A. The reaction is carried out with excess of epichlorohydrin.



Instead of Bisphenol-A, many other compounds with hydroxyl groups such as glycols, glycerols and resorcinols can also be used.

Uses

Epoxy resins have remarkable adhesion. When properly cured, they can yield very tough materials. They are used as adhesives for metals, glass and ceramics. They also find use in floor surfacing, wall panels, cements, mortars, rigid foams, matrix for stained glass windows, surface coatings on household appliances and gas storage vessels.

Summary

- Polymers are very-high-molecular-weight compounds formed by the combination of large number of small repeating units called monomers.
- Polymers are classified on the basis of their origin, monomer composition, chain structure, polymerisation mechanism, nature of molecular forces, tacticity and chemical composition.
- Polymerisation takes place by two mechanisms
 - (i) Addition polymerisation
 - (ii) Condensation polymerisation.
- Addition polymerisation consists of three steps: chain initiation, chain propagation and chain termination.
- Depending on the type of chain initiator, the addition polymerisation can be cationic (chain initiated by cation), anionic (chain initiator is an anion) or free radical polymerisation.

- The three polymerisation techniques are bulk polymerisation, suspension polymerisation and emulsion polymerisation.
- Molecular weight of polymers

$$\text{Number average molecular weight } M_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\text{Weight average molecular weight } M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

- Plastics are a class of polymers that are shaped into hard and tough utility articles by the application of heat and pressure. They are of two types:
 - (i) Thermoplastics
 - (ii) Thermosetting plastics.
- Plastic materials are converted into articles by various methods like compression moulding, transfer moulding, injection moulding, blow moulding and extrusion moulding.
- Rubbers are called elastomers as they can be stretched to at least twice their original length and return to their original length when the deforming force is removed.
- Natural rubber is poly-cis-isoprene. Artificial rubbers can be buna-S, buna-N, butyl rubber, neoprene and thiokol.
- Fibres are semicrystalline polymers having length at least 100 times greater than their width.
- Fibres are spun by melt spinning, dry spinning and wet spinning.
- Glass transition temperature (T_g) is the temperature below which an amorphous polymer becomes hard, brittle and breaks like glass.
- Viscoelastic behavior refers to the behavior of a polymer in which the material on removal of elastic strain does not completely recover its original size.
- Polymers degrade gradually due to heat, radiation and oxidation or by mechanical action.
- Polymer composites are hybrid material formed by the combination of two or more materials to produce a new material having the advantageous properties of the different components, for example, fibre-glass reinforced plastic.
- Adhesives are substances used to bind two or more substances together by surface attachment. Araldite, an epoxy resin, is a common adhesive.

Review Questions

1. Define a polymer. Explain the classification of polymers in detail.
2. What do you understand by functionality of a polymer? Classify the following on the basis of their functionality.
 - (i) Ethylene glycol
 - (ii) Vinyl chloride
 - (iii) Lactic acid
 - (iv) Phenol
3. Explain the mechanism of free radical polymerisation reaction.
4. What are the various steps involved in addition polymerisation? Explain taking the example of cationic polymerisation reactions.
5. What is coordination polymerisation? Explain its mechanism with the help of a suitable example.
6. Explain the following techniques
 - (i) Solution polymerisation
 - (ii) Suspension polymerisation
 - (iii) Bulk polymerisation
 - (iv) Emulsion polymerisation
 - (v) Compression moulding
 - (vi) Transfer moulding
 - (vii) Injection moulding
 - (viii) Blow moulding
 - (ix) Extrusion moulding
7. Explain the number average molecular weight and weight average molecular weight of a polymer.
8. Define plastics. Differentiate between thermoplastics and thermosetting plastics.
9. Explain the preparation, properties and uses of the following polymers
 - (i) Polythene
 - (ii) Polymethylmethacrylate (PMMA)
 - (iii) Teflon
 - (iv) Polyacrylonitrile
 - (v) Polyvinylacetate
 - (vi) Nylon
 - (vii) Bakelite
 - (viii) Urea-formaldehyde resin
 - (ix) Glyptal
 - (x) Polyurethanes
 - (xi) Silicone resins
10. Why are rubbers called elastomers? What is natural rubber? What are the drawbacks of natural rubber?
11. What is vulcanisation of rubber? Explain the advantages of vulcanised rubber over natural rubber.

12. Write the preparation, properties and uses of the following
 - (i) Styrene butadiene rubber
 - (ii) Nitrile rubber
 - (iii) Neoprene
 - (iv) Butyl rubber
 - (v) Polysulfide rubber (thiokol)
13. What is a fibre? How can they be classified?
14. What is spinning? Explain in detail the three principal methods used in spinning.
15. Explain the preparation, properties and uses of the following fibres.
 - (i) Cellulose acetate
 - (ii) Viscose rayon
 - (iii) Terylene
 - (iv) Nylon
 - (v) Acrylics
16. What are polycarbonates? Explain their preparation, properties and uses.
17. What are conducting polymers? How does a non-conducting polymer become conducting? Explain the various uses of conducting polymers.
18. Explain the following
 - (i) Electroluminescent polymers, (ii) Liquid crystalline polymers, (iii) Biodegradable polymers.
19. What are the various mechanical properties of a polymer? Explain.
20. Explain the electrical properties of polymers. How does environment affect the electric properties of polar polymers?
21. What is glass transition temperature (T_g)? Explain its significance and the factors that influence T_g .
22. Explain the viscoelastic behavior of polymers.
23. What do you understand by 'degradation of a polymer'? What are the factors responsible for polymer degradation?
24. Explain the following techniques
 - (i) Hand lay-up technique, (ii) Filament winding technique
 - (iii) Spray lay-up technique, (iv) Pultrusion
25. What is a polymer composite? Explain the properties and uses of FRP and GRP.
26. What are adhesives? Classify them. How are epoxyresins prepared? Explain their end uses.

Multiple Choice Questions

1. A polymer made up of more than one type of monomer is termed as
 - (a) Homopolymer
 - (b) Copolymer
 - (c) Homochain polymer
 - (d) Heterochain polymer

2. Which of the following is a natural polymer
 - (a) Cellulose
 - (b) Polyethene
 - (c) Teflon
 - (d) Nylon
3. Polymer that can be softened on heating and hardens when cooled are
 - (a) Thermosetting plastics
 - (b) Elastomers
 - (c) Fibres
 - (d) Thermoplastics
4. A monomer can form a polymer if its functionality is at least
 - (a) One
 - (b) Two
 - (c) Three
 - (d) Four
5. Polymer that changes reversibly into hard and rigid materials on heating and cannot be re-shaped once it sets is
 - (a) Thermoplastics
 - (b) Fibres
 - (c) Thermosetting plastics
 - (d) Elastomers
6. Which of the following is not a free radical initiator
 - (a) Azo compounds
 - (b) Hydroperoxides
 - (c) Peroxides
 - (d) AlCl_3
7. The number of repeating units (n) in a polymer is called
 - (a) Degree of polymerisation
 - (b) Polydispersity index
 - (c) Molecular weight of polymer
 - (d) Tacticity of a polymer
8. Example of condensation polymer is
 - (a) Polyethene
 - (b) Polyvinylchloride
 - (c) Polyacrylonitrile
 - (d) Terylene
9. The various polymerisation techniques are
 - (a) Bulk polymerisation
 - (b) Solution polymerisation
 - (c) Suspension polymerisation
 - (d) All of the above
10. The molecular weight of a polymer is expressed as
 - (a) Number average molecular weight M_n
 - (b) Weight average molecular weight M_w
 - (c) Both the above
 - (d) None of the above
11. Which of the following is not a thermosetting plastic
 - (a) Bakelite
 - (b) Melamine
 - (c) Epoxyresins
 - (d) Teflon
12. Hollow articles like bottles and hollow toys are manufactured by
 - (a) Compression moulding
 - (b) Transfer moulding
 - (c) Blow moulding
 - (d) Extrusion moulding

13. Plastic moulding process in which the mould has two halves, the upper with a projection called the male die and the lower with a cavity called the female die is
 - (a) Compression moulding
 - (b) Injection moulding
 - (c) Transfer moulding
 - (d) Blow moulding
14. Plexiglass used as a substitute of glass is chemically
 - (a) Polyacrylonitrile
 - (b) Polymethylmethacrylate
 - (c) Polystyrene
 - (d) Polytetrafluoroethylene
15. The trade name of the polymer coated on non-stick utensils is
 - (a) Dacron
 - (b) Orlon
 - (c) Teflon
 - (d) Nylon
16. Bakelite is prepared by the condensation polymerisation of
 - (a) Phenol and formaldehyde
 - (b) Urea and formaldehyde
 - (c) Phenol and acetaldehyde
 - (d) Urea and acetone
17. Glyptal a thermoset polyester is prepared by condensing glycerol (a triol) and
 - (a) Adipic acid
 - (b) Phthalic anhydride
 - (c) Glycol
 - (d) Styrene
18. Cushions for automobiles and furniture are made of
 - (a) Polyurethane
 - (b) Nylon
 - (c) Cellulose
 - (d) Buna-S
19. A polymeric material, which at room temperature can be stretched to at least twice, its original length and returns to its original length as soon as the stretching force is removed is
 - (a) Composite material
 - (b) Elastomer
 - (c) Resin
 - (d) Thermoplastic
20. Natural rubber obtained from the latex of *Hevea brasiliensis* is
 - (a) trans-1, 4-isoprene
 - (b) Butyl rubber
 - (c) cis-1, 4-polyisoprene
 - (d) Neoprene
21. Which of the following is not a synthetic rubber
 - (a) Buna - S
 - (b) Buna - N
 - (c) Neoprene
 - (d) cis-1, 4-polyisoprene
22. Rubber can be vulcanised to improve its properties by heating it with
 - (a) Sulphur
 - (b) Carbon powder
 - (c) Silica
 - (d) Alumina
23. Fibres used for making garments, undergarments, socks, suitings and shirtings are
 - (a) Safety fibres
 - (b) Comfort fibres
 - (c) Industrial fibres
 - (d) Cellulosic fibres

24. Safety fibres are used for making
(a) Clothes (b) Curtains, carpets and seat covers
(c) Tubes, pipes, cars, planes (d) Socks, ropes
25. Which of the following is not a commonly used spinning method
(a) Melt spinning (b) Dry spinning
(c) Wet spinning (d) Solvent spinning
26. Terylene or terene or dacron is a polymer of
(a) Hexamethylene diamine and adipic acid
(b) Ethylene glycol and terephthalic acid
(c) Ethylene glycol and phthalic acid
(d) Phthalic acid and glycerol.
27. Acrylic fibre contains at least 85 percent by weight of
(a) Acrylonitrile monomer (b) Ethylene monomer
(c) Vinyl chloride monomer (d) Styrene monomer
28. Mixers, blenders and food processors are made of a high-performance engineering thermoplastic called
(a) Flexiglass (b) Polycarbonate
(c) Teflon (d) Silicone resin
29. The first known conducting polymer is
(a) Polyacetylene doped with iodine (b) Polyaniline doped with HCl
(c) Polypyrrole doped with BF_4^- (d) Polythiophene doped with ClO_4^-
30. Polyphenylene vinylene is an example of
(a) Conducting polymer (b) Electroluminescent polymer
(c) Biodegradable polymer (d) Liquid crystalline polymer
31. A polymer capable of forming highly ordered regions in liquid phase is
(a) Polyphenylene vinylene (b) Polycarbonate
(c) Kevlar (d) Polyvinylalcohol
32. Which of the following polymers is used in organic light-emitting diodes
(a) Polycarbonate (b) Polyphenylene vinylene (PPV)
(c) Polyacetylene (d) Poly (p-phenyleneterephthalamide)
33. Biodegradable polymers find use in
(a) Orthopaedic fixation devices (b) Controlled drug delivery
(c) Manufacture of plastic bags (d) All of the above
34. The temperature below which an amorphous polymer becomes hard, brittle and breaks like glass is called
(a) Glass transition temperature T_g (b) Melting temperature T_m
(c) Breaking temperature (d) Solidification temperature

35. Materials that do not completely recover their original size when the deforming force is removed are said to exhibit
- (a) Elastic deformation (b) Viscoelasticity
(c) Plastic deformation (d) None of the above
36. Polymers are degraded by
- (a) Heat (b) Radiation
(c) Oxidation (d) All the above
37. Epichlorohydrin and bisphenol-A polymerise to give
- (a) Epoxyresins (b) Polycarbonates
(c) Glyptal (d) Synthetic rubber
38. Polyurethane is obtained from
- (a) p-phenyl di-isocyanate and ethylene glycol
(b) Phenyl isocyanate and ethyl alcohol
(c) Ethylene glycol and terephthalic acid
(d) Bisphenol A + glycol

Solutions

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (a) | 3 (d) | 4 (b) | 5 (c) | 6 (d) | 7 (a) | 8 (d) |
| 9 (d) | 10 (c) | 11 (d) | 12 (c) | 13 (a) | 14 (b) | 15 (c) | 16 (a) |
| 17 (b) | 18 (a) | 19 (b) | 20 (c) | 21 (d) | 22 (a) | 23 (b) | 24 (b) |
| 25 (d) | 26 (b) | 27 (a) | 28 (b) | 29 (a) | 30 (b) | 31 (c) | 32 (b) |
| 33 (d) | 34 (a) | 35 (b) | 36 (d) | 37 (a) | 38 (a) | | |

Chapter 7

LUBRICANTS

7.1 Introduction

A lubricant is a substance introduced between two moving surfaces to reduce friction. This property of reducing friction is termed *lubricity* or *slipperiness* and the process of reducing friction between two moving surfaces by the introduction of lubricants is known as *lubrication*. Before going into what lubrication is, what a lubricant is and how it functions, we need to know what friction is. Friction is the force that resists the relative motion between two bodies in contact. The surfaces of all material, no matter how smooth they appear, are not truly smooth on an atomic scale. They are rough, with sharp and rugged projections called asperities (Fig. 7.1(a)). When two surfaces come in contact with each other, initially, they only touch at a few of these asperity points (Fig. 7.1(b)). When a small load is applied on a metal surface, local high pressure develops at these points (asperities) of contact, which then tend to interlock, thus developing a resistance to motion. When a metal slides, the peaks get broken resulting in wear and tear of the surfaces. Further, if the pressure is high, the asperities deform plastically increasing the contact area between the two surfaces. A sufficiently high pressure leads to the formation of a welded junction between asperities. Additional force is then required to break these junctions. This further adds to the frictional resistance.

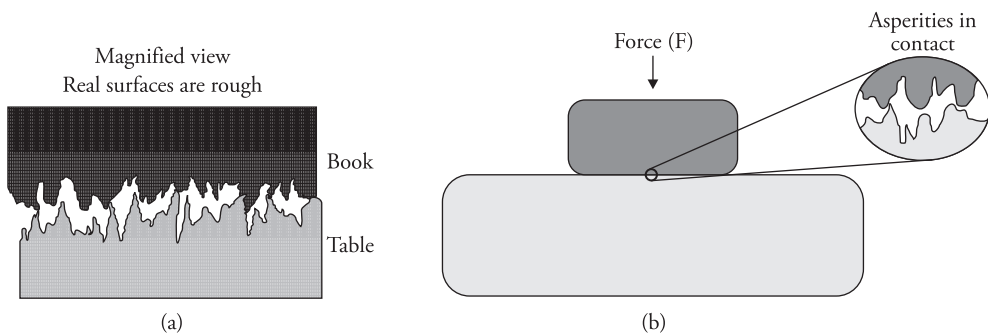


Figure 7.1 (a) Magnified view of a real surface. (b) Contact between two surfaces on application of load

Thus, frictional resistance harms the system in three ways.

- It causes energy loss. Extra work has to be done to overcome the force of friction.
- Friction causes generation of heat in areas in contact. These heated parts may melt and get deformed, leading to seizure (welding of two surfaces due to heat) of the system.
- Breaking of asperities brings about abrasion or surface wear and tear.

7.2 Functions of Lubricants

1. A lubricant reduces frictional resistance by keeping the moving surfaces of a system apart and prevents their direct contact so that the asperities do not interlock.
2. It reduces surface deformation, and wear and tear by keeping the moving surfaces apart.
3. The lubricating oil absorbs the generated heat and acts as a coolant.
4. Lubricants increase the efficiency of the machine.
5. They reduce maintenance cost of machines and increase their life.
6. Lubricants also act as sealants for gases.
7. Lubricant circulation systems carry away debris and contaminants that get introduced into the system.
8. They reduce noise of the machine.
9. They avoid seizure of the moving parts since the use of lubricants minimize the liberation of frictional heat.
10. Lubricants prevent corrosion and rust.

7.3 Mechanism of Lubrication

Depending upon the operating conditions and the lubricant characteristics, lubrication is of the following types:

1. Fluid film or thick film or hydrodynamic lubrication
2. Thin film or boundary lubrication
3. Extreme pressure lubrication

Fluid film or thick film or hydrodynamic lubrication

Hydrodynamic lubrication occurs when the load is low and the speed is high. In this type of lubrication, the two sliding metal surfaces are separated by a thick, continuous unbroken film or layer of the lubricant. The thickness of the fluid film is at least 1000 \AA . The two moving surfaces do not come in contact with each other and the load is taken completely by the oil film. Since the metal surfaces are not in contact with each other, the friction reduces. Whatever friction is there is due to the viscosity or internal resistance of the lubricant. The coefficient of friction in such cases is

as low as 0.001 to 0.03 as compared to 0.5 to 1.5 for sliding metal to metal surfaces in the absence of lubrication.

The basis of hydrodynamic lubrication is the formation of an oil wedge or hydrodynamic wedge between the two moving surfaces. For example, consider the rotation of a shaft with respect to a stationary bearing. The lubricant is introduced in the annular space. In the rest position, the shaft rests at the bottom of the bearing and all the lubricant is squeezed out, resulting in contact between the two surfaces (Fig. 7.2). As torque is applied to the shaft, the fluid pressure forces the surface apart (due to hydrodynamic lift) and the hydrodynamic or oil wedge is developed. Consequently, one surface floats over the other surface without mutual contact.

The lubricants chosen for hydrodynamic lubrication should have minimum viscosity and at the same time remain in its place and separate the sliding surfaces. Hydrocarbon oils are considered to be satisfactory lubricants for fluid film lubrication. However, their viscosity decreases with rise in temperature. Therefore, to maintain their viscosity in all seasons of the year, they are blended with suitable long chain polymers. Moreover, hydrocarbon oils contain a small fraction of unsaturated hydrocarbons which tend to get oxidized forming gummy products. Hence, antioxidants such as aminophenol are also added.

Examples of systems which use hydrodynamic lubrication include the following.

- Delicate instruments like watches and clocks.
- Light machines like sewing machines and scientific instruments.
- Large plain bearings like pedestal bearings and main bearings of diesel engines.

Elastohydrodynamic lubrication Elastohydrodynamic lubrication is similar to hydrodynamic lubrication, but it occurs when the surfaces are in rolling motion relative to each other, like in ball bearings and roller bearings. In elastohydrodynamic lubrication, the pressure is higher and the thickness of the film is much less than hydrodynamic lubrication. It is called elastohydrodynamic lubrication because the film elastically deforms the rolling surface to lubricate it.

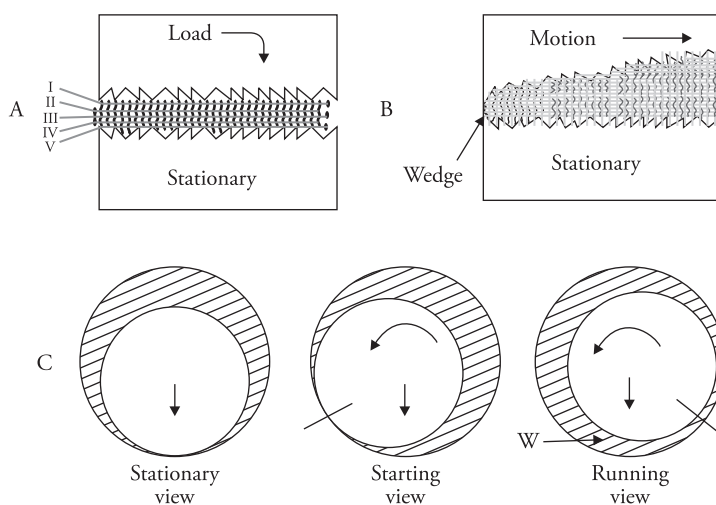


Figure 7.2 Hydrodynamic lubrication

Thin film or boundary lubrication

Boundary lubrication occurs in systems under high load and slow speed. In this kind of lubrication, the lubricating film is thin. It has about the same thickness as the surface roughness such that the high points or asperities on the solid surface are in contact. Figure. 7.3 (a) the load is carried by the surface asperities rather than by the lubricants. The oil film thickness is so small that the effectiveness of the lubricant depends on its oiliness, which is the ability of the lubricant to stick on the surface. The thin film of the lubricant must be adsorbed on the metal surface by physical and chemical forces. Sometimes, the lubricants react chemically with the metal surface forming a thin film of metal soap which acts as a lubricant.

In this type of lubrication, the moving surfaces are not completely separated. However, the points of contact are considerably decreased resulting in lowering of frictional resistance. The thickness of the boundary film may be one or two molecular layers of thickness 20–30 Å (Fig. 7.4). The coefficient of friction in this case is generally 0.05 to 0.15. This friction depends upon the structure and chemical properties of the oil used for lubrication.

Boundary lubrication is undesirable since the metal surfaces are in contact which leads to increased friction, energy loss, wear and tear, and material damage. However, it is inevitable during the operating life of a machine especially when

- A shaft starts moving from rest
- Speed is very slow
- Load is high
- During shut down
- Viscosity of the lubricant is very less
- Under conditions of shock, jerk, etc.

For boundary lubrication, the lubricant should have the following characteristics.

- Its oiliness or the capacity to stick to the metal surface should be good.
- It should have long hydrocarbon chains which increases the lateral attraction between the chains (larger the hydrocarbon chain, greater are the van der Waals forces of attraction).
- It should have polar groups and active groups which adsorb on the metal surface or react chemically with it.
- It should have high-viscosity index and resistance to oxidation.
- Cloud and pour point should be low.

Vegetable oils, animal oils and glycerides of higher fatty acids, and their soaps have good oiliness, for example, oleic acid ($C_{17}H_{33}COOH$) and stearic acid ($C_{17}H_{35}COOH$). Their polar $-COOH$ group reacts with the metal surface to form a continuous film and the hydrocarbon chains of fatty acids are oriented outwards in a perpendicular direction (Figure 7.4)

Graphite and MoS_2 are also used for boundary lubrication. They can bear compression as well as high temperatures. These solid lubricants can be used either alone or as a stable suspension in oil.

Examples of systems using boundary lubrication include the following.

- Lubrication of journal bearing in diesel engines (especially during the starting and stopping of engines).
- Guide and guide shoe in two stroke engines.
- Hydraulic pumps such as the vane pump.
- Valve trains, especially cams and followers.

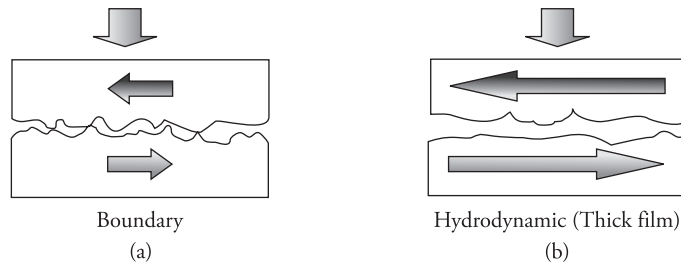


Figure 7.3 (a) Boundary lubrication and (b) Hydrodynamic lubrication compared

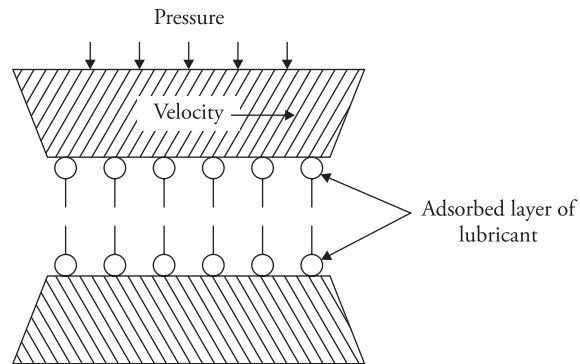


Figure 7.4 Hydrocarbon chains of fatty acids oriented outwards in a perpendicular direction in boundary lubrication

Extreme pressure lubrication

When the moving surfaces are subjected to very high pressure and speed, heat is generated causing the following harmful effects to occur.

- Local high temperature develops resulting in the formation of a welded junction and metal tearing.
- The lubricants fail to stick to the metal surface. They vapourise or decompose.
- Surface deformation and seizure takes place.

To overcome the above difficulties due to extreme pressure conditions, extreme pressure additives are added to the lubricant. The commonly used extreme pressure additives are organic compounds having active radicals or groups such as chlorine (as in chlorinated esters), sulphur (as in sulphurized oils) or phosphorus (as in tricresyl phosphate). The compounds interact with the metal surface at the molecular level to form a protective compound which increases the thermal stability of the metal surfaces. The compounds are generally metallic chlorides, sulphides or phosphides which have high melting points. For example, when additives are added to a lubricant applied on iron and steel, they form iron chloride (MP: 649 °C) or iron sulphide (M.P: 1170 °C). It is important to note that under extreme pressure conditions, the lubricant is not just a film or coating over the metal surface, it is a permanent modification of the metal surface. The surface compound is a few molecule layers thick. The coefficient of friction is 0.1 to 0.4 cm/s. These films remain intact under high pressure and temperature and lubricate the surface. If by chance the film breaks due to the rubbing action of the moving parts, it is immediately replenished. Extreme pressure lubricants find use in aircrafts and spacecrafts.

7.4 Classification of Lubricants

On the basis of their physical state, lubricants can be broadly classified into the following.

1. Liquid lubricants or lubricating oils
2. Semi-solid lubricants or greases
3. Solid lubricants

Liquid lubricants or lubricating oils

Liquid lubricants reduce friction and wear and tear between two metal surfaces by providing a continuous layer between them. They also act as a cooling medium, prevent corrosion and act as a sealing agent. Liquid lubricants can be further subdivided into three types.

- (i) Animal and vegetable oils
 - (ii) Mineral oils or petroleum oils
 - (iii) Blended oil, doped oils or compound oils
- (i) **Animal and vegetable oils** These are extracted from animal and vegetable matter and contain glycerides of higher fatty acids. They are known for their 'oiliness', a property by which they stick to the metal surface even under high temperature and high load. However, they have certain limitations. They are expensive; undergo oxidation to form gummy and acidic products; they oxidize in contact with air and become thick; and they hydrolyse in the presence of moisture in air. They are rarely used for lubrication these days because of these limitations. Rather, they are used as blending agents in mineral oils to improve the oiliness of the latter.

The commonly used animal and vegetable oils are olive oil, mustard oil, castor oil, palm oil, rapeseed oil, whale oil etc.

- (ii) **Mineral oils or petroleum oils** These oils are obtained by the fractional distillation of crude petroleum. On being subjected to vacuum distillation, the heavy residual fraction yields lubricating oil. The hydrocarbon chain is 12 to 50 carbon atoms long. They are widely used as lubricants because they are cheap, abundant and stable under working conditions. They are not readily hydrolysed. However, they have poor oiliness as compared to vegetable oils. Their oiliness is increased by blending them with vegetable oils.
- (iii) **Blended oils** Blended oils are termed as doped oils or compounded oils. No single oil can serve as a satisfactory lubricant under all conditions. Hence, their properties are improved by adding certain additives. This phenomenon is called 'blending'. The different additives employed are as follows.
- (a) **Antioxidants or inhibitors** They retard the oxidation of lubricating oils by getting themselves preferentially oxidized. Antioxidants are added in lubricants used in internal combustion engines. Examples include aromatic phenolic or amino compounds.
 - (b) **Oiliness carriers** They increase the oiliness of the lubricant. These carriers are added in lubricants used in boundary lubrication. Examples include vegetable oils like castor oil, mustard oil and fatty acids like oleic acid, palmitic acid, stearic acid, etc.
 - (c) **Viscosity index improvers** They increase the viscosity index and are added in lubricants used in machines working under a broad temperature range. Example includes hexanol.
 - (d) **Pour point depressants** They reduce the pour point of the oil. Examples include alkylated naphthalene, phenolic polymers and polymethacrylates.
 - (e) **Detergents and defloculents** They neutralise sludge and varnish precursors and keep the surface deposit free by maintaining them in soluble form. Examples include calcium and barium salts of phosphates and sulphonates.
 - (f) **Dispersants** They prevent and retard sludge formation. Dispersants are added in lubricating oils used in internal combustion engines. Examples include high-molecular-weight amides and amide polymers.
 - (g) **Metal deactivators** They stop the catalytic effect of metals on the oxidation states. Examples include amines, sulphides or phosphides.
 - (h) **Antifoaming agents** They prevent the formation of stable foams. Examples include glycol, glycerol and silicon polymers.
 - (i) **Rust and corrosion inhibitors** They protect the metal from corrosion, for example, organometallic compounds, metal phenolates, basic metal sulphonates, fatty acids and amines.
 - (j) **Extreme pressure additives** They enable the lubricant to function under the conditions of high temperature and pressure, for example, sulphurized fats, phosphorus compounds, etc.
 - (k) **Abrasion inhibitors** They provide abrasion resistance, for example, tricresyl phosphate.
 - (l) **Emulsifiers** They help in the formation of emulsions of lubricating oils with water, for example, sodium salts of sulphonic acids and sodium salts of organic acids.

Semi-solid lubricants

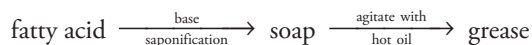
Greases are the most common examples of semi-solid lubricants. They are oils made semi-solid by adding a thickening agent. The thickeners dispersed in the lubricating oil produce a stable and colloidal structure or gel. In fact, greases contain three basic active ingredients – a lubricating oil, additive and thickeners (Table 7.1). Thickeners are mainly special soaps of lithium, sodium, calcium, barium, etc. Non-soap thickeners like carbon black, clay, asphaltene and siloxane are also used.

Table 7.1 Basic ingredients of grease

Lubricating oil	Thickener	Additive
Petroleum oil	Soap of Li, Na, Ba, Ca, Al	Antiwear, antioxidant, rust and corrosion resistant, viscosity index improver, pour point depressers, extreme pressure additives, etc.
Polyglycols		
Polyalpha olefins	Non-soap (inorganics) clay, graphite, silica,	
Vegetable oils	carbon black	

Preparation of greases

Greases are prepared by the *saponification* of fat (such as tallow or fatty acid) with alkali (NaOH, Ca (OH)₂, etc.) followed by the addition of hot lubricating oil with constant stirring



The consistency of the grease depends upon the quantity of oil added. Mineral oil plays an important role in determining the performance of the grease. The nature of soap used decides the consistency of the grease, the temperature up to which it can be used and its resistance to water and oxidation. Greases are classified on the basis of the soap used in their manufacture (Table 7.2).

Table 7.2 Classification of greases

Type of grease	Chemical composition	Characteristic properties
Calcium base greases	Emulsions of petroleum oils with calcium soaps	Insoluble in water hence water resistant. Since oil and soap separate above 80 °C, these greases are used up to 80 °C. They are suitable for water pumps, tractors, etc.
Soda-based greases	Petroleum oils, thickened by mixing sodium soap	Not water resistant because sodium content of soap is soluble in water; they can be used up to 175 °C; they are suitable for use in ball bearings where the lubricants gets heated due to friction
Lithium-based greases	Petroleum oil thickened by mixing lithium soap	Water resistant but can be used up to 15 °C only. They are expensive
Axle greases	Resin and fatty oils mixed with lime or any heavy metal hydroxide (talc and mica are added as fillers)	Water resistant, cheapest of all greases; they find use in equipments working under high loads and low speeds
Non-soap greases	Mineral oil with solids like graphite, carbon black and soapstone	Used in rail axle boxes, machine bearings, tractors, rollers, etc.

Applications

1. Greases are generally used in textile mills, paper mills and mills of edible articles where use of liquid lubricants can cause contamination of the products by spilling or dripping.
2. Machines like rail axle boxes work at slow speed and high pressure, intermittent operation and sudden jerks. In such conditions, oil cannot remain in its place.
3. In bearing and gears working at high temperatures.
4. Used in bearings which need to be sealed against the entry of dust, grit and moisture.

However, there are certain limitations of greases. These are as follows.

1. Their coefficient of friction is much higher than that of lubricating oils; therefore, wherever possible lubricating oils are preferred over greases.
2. Compared to lubricating oils, greases cannot dissipate heat effectively from the bearing.
3. Greases cannot be used in the presence of water because the fibre structure of the thickeners is adversely affected by water and the grease undergoes degradation.

Solid lubricants

Solid lubricants are used in places where liquid and semi-liquid lubricants fail to give satisfactory results. They offer lubrication at

- Very high temperatures and pressure where other lubricants fail to stay in their position.
- Solid lubricants like MoS_2 are used in vacuum where liquid and semi-solid lubricants are ineffective.
- Solid lubricants are used in industries where entry of dust is not acceptable.

The most common solid lubricants are graphite and molybdenum disulphide. Their lubrication properties are due to their layered or lamellar structures. The layers are held together by weak van der Waals forces and hence can easily slip over each other.

- (i) **Graphite** Graphite consists of a stack of carbon atom sheets, each sheet containing a hexagonal arrangement of atoms. Each carbon is sp^2 hybridised. The adjacent layers are separated by a distance of 3.4 \AA and are held together by weak van der Waals forces. Hence, graphite is soapy and slippery by nature. It is non-inflammable and is not oxidized in air below 375°C . Graphite is used either as a powder or as a suspension or as grease. In dry form, it is an effective lubricant additive because of its lamellar structure. The lamellas orient parallel to the surface in the direction of motion. It can also be used as a suspension with oil or water. Its suspension in oil is called 'oildag' (*dag* meaning deflocculated adhesion graphite). Oildag finds use in internal combustion engines because it provides a tight fit contact by forming a film between the piston and the rings. Suspension of graphite with water is called 'aquadag'. It is prepared using tannin as an emulsifying agent. Aquadag is used where oil free lubricant is required.

Graphite is best suited for lubrication in air. Water vapour is essential for graphite lubrication. Water is adsorbed; it reduces bonding energy between the hexagonal planes of graphite. Graphite cannot be used in vacuum because it needs water vapour to lubricate (for figure, refer to Fig. 11.48, Chapter Solid State).

Applications Graphite is commonly used in air compressors, food industry, ball bearings, railway track joints, etc.

- (ii) **Molybdenum disulphide (MoS_2)** It has a sandwich like structure in which the molybdenum atoms lie between two layers of sulphur atoms (Fig. 7.5). MoS_2 has low shear strength in a direction parallel to the layers due to poor interlaminar attraction. Hence, it has low coefficient of friction. It is stable in air up to 400°C . MoS_2 has excellent adhesion, high load carrying capacity and protection against corrosion. However, it cannot be used in wet environment as moisture increases friction. MoS_2 is an excellent lubricant in vacuum, hence, it finds use in space vehicles. A solid film lubricating surface useful for space vehicles is made from 70% MoS_2 + 7% graphite bonded with 23% silicates. It can withstand extreme temperatures, low pressure and nuclear radiations.

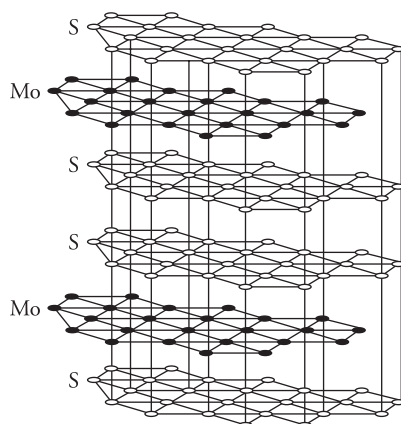


Figure 7.5 Sandwich like structure of MoS_2

Besides graphite and MoS_2 , other common solid lubricants are soapstone, talc, mica, polytetrafluoroethylene (PTFE), hexagonal boron nitride (called white graphite and is used in space vehicles), etc.

7.5 Synthetic Lubricants

Conventional lubricants obtained from natural oils are a cocktail of hydrocarbons and in spite of aggressive solvent base refining, they contain many organic as well as inorganic impurities. This causes oxidation, acid formation and promotes the formation of sludge in the lubricants.

Synthetic lubricants are engineered products. They are synthesized by chemical reactions. All the components are of high purity and as a result, the end product formed is a pure compound which is less vulnerable to oxidation and breakdown. It does not emulsify and produce undesirable products. Synthetic lubricants are tailor made and have a unique combination of properties like the ability to perform satisfactorily over a wide range of temperature, high-viscosity index, resistance to hydrolysis, long service life even in reactive environment, etc.

The commonly used synthetic lubricants are as follows.

- (i) **Dibasic esters** di-2-ethyl hexylsebacate is the most widely used dibasic ester. It has a satisfactory performance from $(-50^{\circ}\text{C}$ to 230°C . They have low volatility, a high-viscosity index and high temperature stability and are non-corrosive, non-toxic and stable to hydrolysis. These are generally used in jet engines and military equipments.
- (ii) **Halogenated hydrocarbons** Although halogenated hydrocarbons have a low-viscosity index, they are good for extreme pressure lubricating properties. However, they are costly. They find use in submarines due to their low inflammability, resistance to oxygen, H_2O_2 and chemicals.
- (iii) **Polyglycols and their derivatives** They can be water soluble or insoluble depending upon the length of the carbon chain. Common examples are polyethylene glycol, polypropylene glycol, higher polyalkylene oxides, polyglycidyl ethers, etc.
Polyglycidyl ether is water insoluble but can adsorb water. These lubricants have low pour points, high-viscosity index, do not affect rubber and other gasket materials and are cheap. Polyethylene oxides however undergo thermal decomposition at high temperature and hence cannot be used at elevated temperatures. These lubricants find use in combustion engines, gears, compressors and pumps.
- (iv) **Organophosphate esters** They are fire-resistant and are used for extreme pressure lubrication.
- (v) **Silicones** They are excellent synthetic lubricants because of their resistance to oxidation up to 200°C , high-viscosity index, chemical inertness, etc. Silicon fluids are generally used for rubber and plastic surfaces such as bushings, bearings, etc. They are also used as moisture repellent lubricants for clocks, timers and other electronic devices.
- (vi) **Organic amines, imines and amides** They possess low pour point, high-viscosity index and can be used in the temperature range $(-50^{\circ}\text{C}$ to 250°C .

7.6 Lubricating Emulsions

An emulsion is a colloidal solution consisting of more than one immiscible liquid dispersed in another in the form of droplets (for details, refer to the chapter on Surface Chemistry Section 14.14).

Emulsion (oil in water or water in oil type) can also be used for lubrication. In machining operation like milling, boring, turning, cutting, the tool employed gets heated to a high temperature. This may cause oxidation and subsequent corrosion of metal. In order to prevent overheating, effective cooling and lubrication is required. Oil in water emulsions are used as cooling and lubricating liquids in cutting tools. The oil lubricates and the water acts as a coolant. Fatty acids such as lard oil and sperm oil are very good for cutting tools. Water in oil emulsions are prepared by mixing water and oil containing 1 to 10% of water insoluble emulsifiers like alkaline earth metal soaps. They find use as compressors and pneumatic tool lubricants as the water evaporates and gives an internal cooling effect.

7.7 Properties of Lubricants

Viscosity

Viscosity is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. A liquid in a steady state of flow on a surface may be supposed to consist of a series of parallel layers moving one above the other. Each layer moves faster than the lower layer due to internal friction.

Consider two layers of a liquid which are at a distance d , moving with a velocity difference v . Then, the force per unit area (F) required to maintain this velocity difference is given by

$$F = \frac{\eta v}{d}$$

where η (eta) is the proportionality constant known as the coefficient of viscosity. This constant η is characteristic of a particular liquid at a given temperature and decreases with increase in temperature. If $v = 1 \text{ cm/s}$ and $d = 1 \text{ cm}$, then

$$F = \eta,$$

Hence, coefficient of viscosity (η) may be defined as *the force per unit area required to maintain a velocity difference of unity between two parallel layers separated by unit distance*.

Absolute viscosity It may be defined as the tangential force per unit area required to maintain a unit velocity gradient between two parallel layers. Absolute viscosity is denoted by η (eta). Its unit in CGS system is poise. Poise being a bigger unit, centipoise is generally used. One centipoise = 0.01 poise.

Absolute kinematic viscosity It is the ratio of absolute viscosity to density of any fluid. Absolute kinematic viscosity is denoted by V . Its unit in CGS system is stoke. The smaller unit centistoke is commonly used. 1 centistoke = 0.01 stoke.

Centistoke = centipoise / density

Significance of viscosity Viscosity is a very significant property used to determine the quality of a lubricant under a given set of operating conditions. If the machine is moving at a slow speed under heavy load, lubricants of high-viscosity are preferred because low-viscosity lubricants will be squeezed out of the moving parts. On the other hand, in light machines like sewing machines, clocks, etc, low-viscosity lubricants are selected as high-viscosity oil will cause jamming of the machine parts.

Effect of temperature on viscosity Viscosity of a lubricant decreases with the rise in temperature. Hence at high temperature, the lubricant might be squeezed out of moving parts. Therefore, it is essential that the viscosity of the chosen lubricant should not vary much with the change in temperature – in this way, the lubricant remains in its place (between the moving parts) and can be used continuously at high temperatures as well. The rate of change of viscosity with temperature is measured on an arbitrary scale known as the *viscosity index*.

Viscosity index (VI) It is an empirical scale used to measure the change of viscosity of oil with temperature. The VI is defined as the average decrease in viscosity of oil per degree rise in

temperature between 100 °F and 210 °F. If the viscosity of a lubricant decreases rapidly with the rise in temperature, it is said to have low-viscosity index. On the other hand, if the viscosity does not change much with the increase in temperature, then the lubricant is said to have high-viscosity index.

Determination of viscosity index

Two types of standard oils are used to determine VI.

- Paraffinic-based Pennsylvanian oils whose viscosity does not vary much with temperature. These are known as H-oils and have been assigned VI = 100.
- Naphthenic-based Gulf oils which show a large change in viscosity with temperature. These are known as L-oils and have been assigned VI = 0.

To determine the viscosity index of a test oil

- The viscosity of the test oil is found experimentally at 100 °F and 210 °F. Let it be U and V , respectively.
- From the list of H-oils, that oil is selected whose viscosity at 210 °F is the same as that of the test oil at 210 °F and its corresponding viscosity at 100 °F is read off. Let it be H .
- Similarly, from the list of L-oils, that oil is selected whose viscosity at 210 °F is the same as that of the test oil at 210 °F and again its corresponding viscosity at 100 °F is read off. Let it be L . VI is given by the formula

$$VI = \frac{L - U}{L - H} \times 100$$

where U = Viscosity of the test oil at 100 °F (38 °C)

H = Viscosity of H-oil at 100 °F having the same viscosity at 210 °F (99 °C) as the viscosity of the test oil at 210 °F.

L = Viscosity of L-oil at 100 °F. Viscosity of test oil and L-oil at 210 °F is the same.

The viscosity index depends directly on the molecular structure of the compound. Linear molecules have high-viscosity index. Branched molecules have low-viscosity index because branches prevent the alignment of the neighbouring molecules.

The viscosity index of lubricating oil can be increased by adding organic polymers like polyisobutylene, n-hexanol, etc. These polymers are partially soluble in the lubricant at low temperatures. The solubility of the polymer increases with the rise in temperature. Therefore, as temperature increases, two opposite effects occur.

- Viscosity of the lubricating oil decreases.
- Solubility of the polymer in the lubricating oil increases, resulting in increase in its viscosity.

Because of these two opposing effects, the viscosity of the lubricant remains constant or in other words, the viscosity index of the lubricant increases.

Solved Examples

1. An oil sample under test has the same viscosity as that of the standard Gulf oil (low-viscosity standard) and Pennsylvanian oil (high-viscosity index standard) at 210 °F. Their viscosities at 100 °F are 61, 758 and 420 s, respectively. Calculate the viscosity index of the oil sample.

Solution

$$L = 758 \text{ s}, H = 420 \text{ s}, U = 61 \text{ s}$$

$$VI = \frac{L-U}{L-H} \times 100 = \frac{758-61}{758-420} \times 100 = 206.2$$

Practice problems

1. An oil of unknown viscosity index has a redwood viscosity of 64 s at 210 °F and 564 s at 100 °F. The low-viscosity standard (Gulf oil) possess a redwood viscosity of 64 s at 210 °F and 774 s at 100 °F. The high-viscosity standard (Pennsylvanian oil) has a redwood viscosity of 64 s at 210 °F and 414 s at 100 °F. Calculate the viscosity index of the unknown oil. [Ans 58.33]
2. An oil of unknown viscosity index has a viscosity of 60 s at 210 °F and 600 s at 100 °F. The high-viscosity index standard (i.e., Pennsylvanian oil) has a viscosity of 60 s at 210 °F and 500 s at 100 °F. The low-viscosity index standard (Gulf oil) has a viscosity of 60 s at 210 °F and 800 ss at 100 °F. Calculate the viscosity index of the unknown oil. [Ans 66.67]

Measurement of viscosity

The instrument used to measure viscosity is called a viscometer. Different types of viscometers are in use. They all work on the principle of allowing a fixed volume of oil to flow from a standard orifice at a fixed height and measuring the time of flow in seconds. The instruments commonly used are as follows.

- **Redwood viscometer** A Redwood viscometer measures the time required for 50 mL of the oil to pass through its orifice.
- **Saybolt viscometer** A Saybolt viscometer measures the time required for 60 mL of the liquid to pass through its orifice.

The viscosity determined by the above two methods is expressed in redwood seconds and saybolt universal seconds, respectively.

A brief description of a Redwood viscometer which is commonly used in our country is given here.

Based on the size of the orifice, Redwood viscometers are of two types – Redwood viscometer no. 1 and Redwood viscometer no. 2. Redwood viscometer no 1 with an agate jet of diameter 1.62 mm and length 10 mm is used for measuring the viscosity of thin lubricating oils. On the other hand, Redwood viscometer no. 2 is used for measuring the viscosity of thick lubricating oils like fuel oils, and has a jet of diameter 3.8 mm and length 15 mm.

Construction of a Redwood viscometer no. 1

It consists of the following parts (Fig. 7.6).

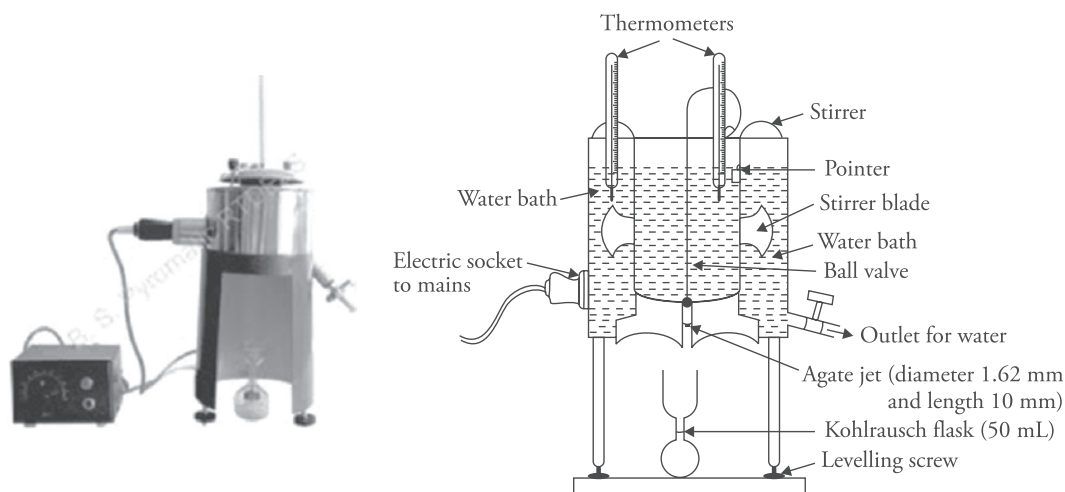


Figure 7.6 Redwood viscometer

- (i) **Oil cup** It is a silver plated brass cup (90 mm in height and 46.5 mm in diameter) with its upper end open. At the lower end, it has an orifice (length = 10 mm; diameter = 1.62 mm). The orifice is opened and closed with the help of a ball valve. The upper open end of the cup is closed with a lid having holes, one for the thermometer to record the temperature of the oil and the other for the ball valve. The side wall of the cup is provided with a pointer which is stout, tapered and pointing towards the upper side of the cup. The oil is filled till the tip of the pointer.
- (ii) **Heating bath** The oil is surrounded by a copper bath containing water. It is provided with a tap for emptying the water. It also bears an element for heating purposes. A thermometer is inserted to indicate the temperature of the water. The outer cylinder is also provided with a stirrer.
- (iii) **Spirit level** The apparatus rests on three legs provided with levelling screws at the bottom. The spirit level on the lid is used for levelling of the apparatus.
- (iv) **Kohlrausch flask** It is a calibrated flask placed at the bottom of the orifice used for collecting 50 mL of the oil sample.

Working The apparatus is levelled and oil is filled till the tip of the pointer taking care to close the orifice with the ball valve. The oil is heated. When the oil reaches the desired temperature, the ball valve is removed and the time taken for the flow of 50 mL of the oil sample is noted. This gives the redwood viscosity in seconds at the test temperature.

Conversion formula

The Redwood viscosity can be converted into kinematic viscosity using the formula

$$V = At - \frac{B}{t}$$

where V = kinematic viscosity of the oil in centistokes.

t = time of the flow in seconds

A and B are instrument constants. The value of

$A = 0.264$, $B = 190$ when $t = 40$ to 85 s

$A = 0.247$, $B = 65$ when $t = 85$ to 2000 s

Flash and fire point

Flash point is the minimum temperature at which the oil vapour–air mixture ignites for a moment, producing a spark when a small flame is brought near it. Fire point is the minimum temperature at which the vapours of the oil burn continuously for at least 5 s when a small flame is brought near it. Generally, the fire point is $5\text{--}40^\circ$ higher than the flash point. Flash and fire point is determined with the help of a *Pensky–Marten apparatus* (Fig. 7.7) which consists of the following parts.

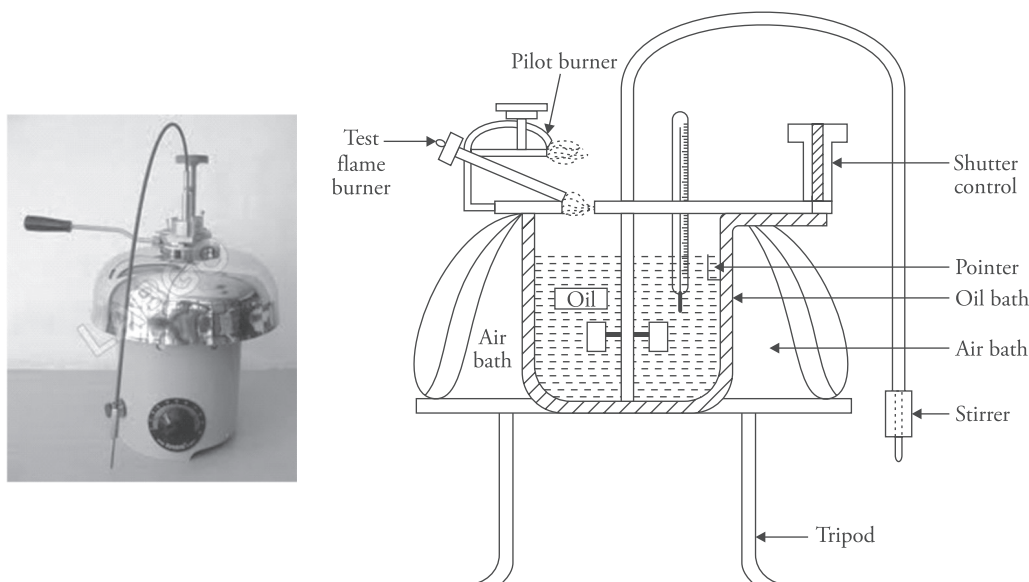


Figure 7.7 *Pensky–Marten apparatus*

- (i) **Oil cup** It is made of brass (5.5 cm deep and 5 cm in diameter). It has a lid provided with four openings of standard dimensions. One opening is for the thermometer, the second is for introducing the test flame, the third opening is for the stirrer and the fourth for the passage of air. The oil cup has a pointer on the side wall.
- (ii) **Shutter** It is provided at the top of the cup. By moving the shutter, the opening in the lid opens and the test flame is inserted inside the oil cup, thereby bringing it over the oil surface.
- (iii) **Air bath** The oil cup is surrounded by an air bath which is heated either by a gas burner or by an electric element.
- (iv) **Pilot burner** As the test flame is introduced in the opening, it extinguishes, but when it returns to its original position, it is automatically kindled by the pilot burner near the test flame.

Working The oil sample is filled in the cup till the tip of the pointer. A thermometer is inserted, the oil is heated and the stirrer is worked. The test flame is inserted inside the oil cup at every 1 °C rise in temperature. The temperature at which a flash (combination of light and sound) is observed is noted as the flash point and the temperature at which the flame continues to burn for at least 5 s is the fire point of the oil.

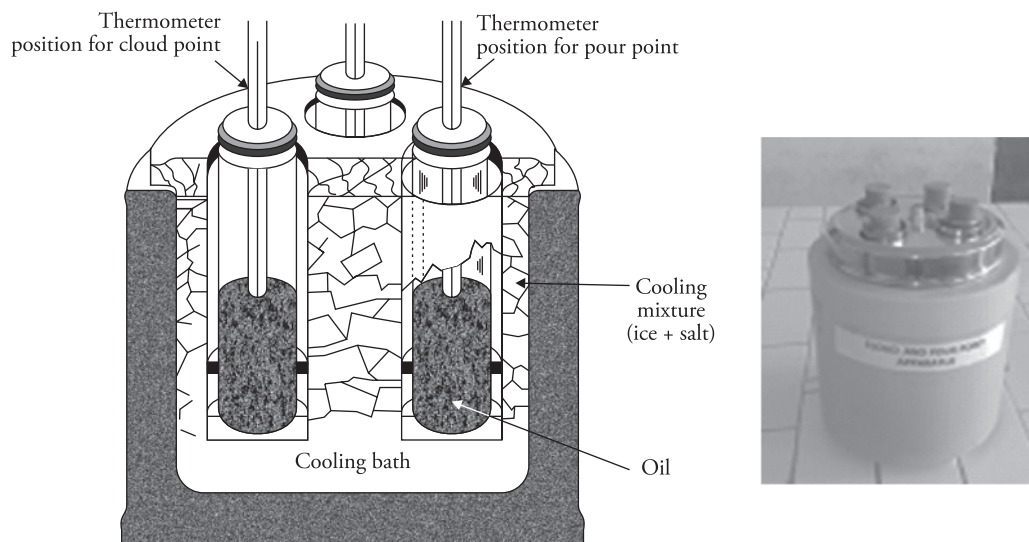
Significance Flash and fire point has no bearing on the lubricating properties of the oil but measures the fire hazards of the lubricants. A good lubricating oil should have flash and fire point at least 5–10° above the working temperature of the machine. It safeguards against the risk of fire during the operation of machine at high temperatures.

Cloud and pour point

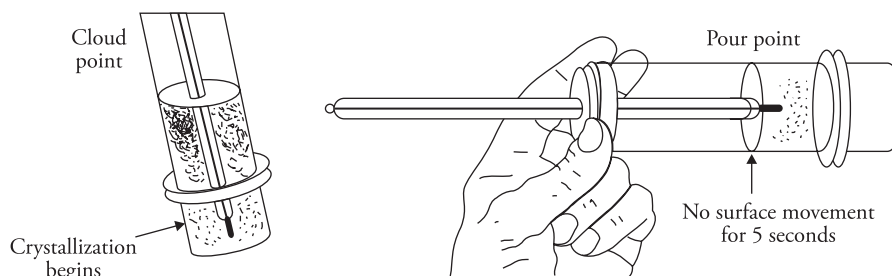
When oil is cooled slowly, the temperature at which it becomes cloudy or hazy is called the *cloud point* and the temperature at which it stops flowing when the tube is made horizontal (tilted) is called the *pour point*. Hence, the pour point refers to the maximum temperature at which a lubricant continues to flow. Below the pour point, the oil thickens and does not flow freely. Cloud and pour points can be determined with the help of a cloud and pour point apparatus.

Construction and working

The apparatus consists of a flat bottom tube (about 2 cm high and 3 cm in diameter) enclosed in an air jacket. The tube is half filled with oil and a thermometer is introduced in the oil. It is then placed in a freezing mixture (ice + NaCl or CaCl₂). As the oil cools, the temperature falls continuously. With every degree fall in temperature, the glass tube is withdrawn from the air jacket and observed. The temperature at which cloudiness or haziness appears is the cloud point of the lubricating oil (Fig. 7.8). After recording the cloud point, the tube is now withdrawn at every three degree fall of temperature. It is tilted and observed. The temperature at which the oil does not flow even when kept horizontal for at least 5 s is reported as the pour point of the lubricant (Fig. 7.8(b)).



(a) Cloud point measurement



(b) Pour point measurement

Figure 7.8 • *Cloud and pour point apparatus***Significance**

Like flash and fire point, this too does not have a bearing on the lubricating properties of the oil. However, it signifies the suitability of the lubricant in cold conditions. Machines working in cold conditions should use a lubricant with low cloud and pour point, otherwise, the lubricant will solidify causing the jamming of the machine.

Aniline point

Aniline point of an oil is the temperature at which equal volumes of oil and aniline are just miscible. Aniline point is related to the percentage of aromatics in the oil. The lower the aniline point, the higher is the percentage of aromatics in the oil. Aromatic hydrocarbons are good solvents for natural rubbers and certain synthetic rubbers. The presence of these in oils will deteriorate rubber sealing and packing by dissolving them. A higher aniline point is therefore desirable.

To determine the aniline point, equal volumes of oil sample and aniline are mixed mechanically in a test tube and heated till a homogeneous solution is obtained. The tube is placed in a thermostat and cooled slowly. The temperature at which the two phases separate out is called the aniline point.

Steam emulsion number

When water enters an oil system, it forms an emulsion. These emulsions have poor lubricating properties and cause abrasion and wearing out of the lubricated parts of the machinery.

Hence, a good lubricating oil should form an emulsion with water, which breaks off quickly. The steam emulsion number (SEN) is determined by ASTM test. In this, 20 mL of oil is taken in a test tube and steam at 100 °C is bubbled in, till the temperature rises to 90° C. The tube is kept in a bath maintained at 90 °C and the time in seconds, when the oil and water separates out is noted. This time in seconds taken for oil and water to separate out into distinct layers is called an SEN. A good lubricant should have a low SEN.

Neutralisation number

It is an indication of the acidic and basic impurities in the lubricating oil. It is expressed either as a *total acid number* (TAN) which is the number of milligrams of KOH needed to neutralise any acid in one gram of oil or the *total base number* (TBN), which is the number of milligrams of HCl needed to neutralise any base in one gram of oil. Determination of acidity is more common and is expressed in terms of acid value or acid number. A known weight of oil is dissolved in a neutral alcohol and titrated against 0.1 N KOH using phenolphthalein as the indicator.

$$\text{Acid value} = \frac{\text{mL of KOH used} \times \text{normality} \times 56}{\text{Weight of the oil taken in g}}$$

Acid value of a lubricant should be less than 0.1. A value greater than 0.1 indicates that the oil has been oxidized.

Saponification number

An ester on alkaline hydrolysis gives alcohol and sodium or potassium salt of an acid. The saponification number is defined as the number of milligrams of KOH required to saponify the fatty acid present in 1 gram of oil. It is determined by refluxing a known quantity of oil with a known excess of potassium hydroxide solution and titrating the unused alkali against an acid.

Iodine value

It is a measure of the degree of unsaturation and the tendency of a fatty oil to absorb oxygen. Iodine value is defined as the number of milligrams of iodine absorbed by one gram of the oil. It is determined by adding a measured excess of a solution of iodine bromide in glacial acetic acid to a weighed quantity of oil dissolved in CCl₄ or acetic acid. The addition of the halogenating agent to the double bond is allowed to proceed to completion. The unused IBr is then back-titrated against a standard hypo solution using starch as an indicator.

Carbon residue

Lubricating oils contain high percentage of carbon in combined form. On being subjected to high temperature, they decompose and form a carbonaceous deposit. Oils which deposit a minimum amount of carbon are preferable. To determine the carbon residue, a bulb containing known weight of oil sample is heated to a temperature of 500 °C. The weight of the carbon residue formed is determined after cooling. The carbon residue is given by

$$\% \text{ carbon residue} = \frac{\text{Weight of residue in crucible/bulb}}{\text{Weight of original oil sample}} \times 100$$

7.8 Selection of Lubricants for Different Types of Machinery

In selecting a lubricant for a particular machine, various parameters have to be kept in mind. Lubricant selection is based on knowledge and experience. Tribology – the science of friction, lubrication and wear plays a vital role in the selection of lubricant. While selecting the lubricant, a lubrication engineer (tribo-engineer) should take into account the type of motion (sliding or rolling), speed of the machine, temperature condition, load (light or heavy) and the operating environment which includes moisture, air, oxygen, chemicals, liquids, vapours, etc.

Selection of lubricants for a few typical jobs is illustrated in Table 7.3.

Table 7.3 Selection of lubricants for a few typical jobs

Lubricant application	Properties of special interest in the lubricant	Recommended lubricant
Transformers	High resistivity, high dielectric strength, low-viscosity, high oxidation resistivity	Highly refined and moisture free mineral oils
Gears	Subjected to extreme pressure hence should have good oiliness, high film strength, oxidation resistance, high load carrying capacity	Thick mineral oils containing extreme pressure additives like metallic soaps, chlorine, sulphur or phosphorus compounds
Steam turbine	High-viscosity, high metal wetting, high temperature resistance, resistance to hydrolysis and oxidation	Steam refined paraffin base mineral oil compounded with fixed oil (vegetable and animal oils)
Internal combustion engines	High-viscosity index, high thermal stability	Petroleum oils containing additives
Delicate instruments like watches, clocks, sewing machines, scientific instruments	They are not exposed to high temperature, high load or water	Thin vegetable and animal oils like palm oil, neat oil, etc.

Cutting tools	Cool the tool, reduce wear, reduce power consumption by lubricating action, low-viscosity, prevent rust and fine finish	(i) <i>Heavy cutting</i> : Mineral oils containing additives like fatty oils, sulphurized fatty oils and chlorinated compounds (ii) <i>Light cuttings</i> : oil emulsions
Spindles in textile industry	Move at very high speeds	Thin oils containing additives like oxidation and rust inhibitors
Refrigeration system	Low pour point, low-viscosity, low cloud point	Naphthalene-based oils

Summary

- Lubricant is a substance introduced between two moving surfaces to reduce friction – a force which opposes the motion of any object.
- Apart from lubricating the moving surfaces, a lubricant acts as a coolant, reduces wear and tear, acts as a sealant for gases, reduces noise of the machine, reduces maintenance cost and increases the life of a machine.
- A good lubricant should have good oiliness (stick to the metal surface), its viscosity should be moderate, its ignition temperature should be high, freezing point should be low, it should not oxidize or hydrolyse in air.
- Lubrication which occurs by the formation of a thick film between the metal surfaces is called hydrodynamic or fluid film lubrication.
- In boundary lubrication, when the load is high and speed is slow, a thin film is formed between the metal surfaces. The film remains in its place due to adsorption on the metal.
- Extreme pressure lubrication occurs when extreme pressure additives like organic groups having chlorine, sulphur or phosphorus react with the metal surface forming a compound of high melting point.
- On the basis of their physical state, lubricants are classified as liquid lubricants, semi-solid lubricants and solid lubricants.
- Viscosity is the property by virtue which a liquid opposes its own flow. A good lubricant should have moderate viscosity and a viscosity which should not vary with temperature (viscosity index should be high).
- Viscosity is measured with the help of a Redwood viscometer and Saybolt viscometer.
- The temperature at which a lubricant produces flash is its flash point and the temperature at which it burns continuously for 5 s is called its fire point. Flash and fire points are measured by a Pensky–Martens apparatus. It signifies the fire hazards of a lubricant.

- The temperature at which a lubricant become cloudy is called its cloud point and the temperature at which it stops flowing is the pour point. They can be found with the help of a cloud and pour point apparatus. These points signify the suitability of a lubricant under cold conditions.
- Other important properties of lubricating oils are aniline point, emulsification, neutralisation number, saponification number, iodine value and carbon residue.

Review Questions

1. Define a lubricant. What are the functions of a lubricant and what are the qualities of a good lubricant?
2. What is hydrodynamic lubrication? Explain the phenomenon with the help of a suitable diagram.
3. How does lubrication occur by thin film or boundary lubrication? Distinguish between fluid film and boundary lubrication.
4. Write a short note on extreme pressure lubrication.
5. Classify lubricants.
6. What do you mean by blended or compounded oil? What are the various additives used to impart desirable properties to lubricants?
7. What are greases? Explain the different type of greases and also write down their advantage over liquid lubricants. What are the limitations of greases?
8. What are synthetic lubricants? Synthetic lubricants have an added advantage over natural lubricants. Explain.
9. What is viscosity? How will you determine the viscosity of a lubricating oil with the help of Redwood viscometer no. 1?
10. How does viscosity vary with temperature? Explain the determination of viscosity index of a lubricating oil. Suggest measures to improve the viscosity index of an oil sample.
11. What is flash and fire point? How can you determine the flash and fire point of a lubricant with the help of a Pensky–Marten apparatus?
12. Write short notes on
 - (i) Cloud and pour point
 - (ii) Emulsification
 - (iii) Aniline point
 - (iv) Neutralisation number
 - (v) Iodine value
 - (vi) Carbon residue
 - (vii) Saponification number.

Multiple Choice Questions

- The functions of a lubricant are
 - It reduces friction
 - It acts as a coolant
 - It acts as a sealant for gases
 - All of the above
- Delicate instruments like watches, clocks and light machines like scientific instruments and sewing machines have which type of lubrication
 - Thick film or hydrodynamic lubrication
 - Thin film or boundary lubrication
 - High-pressure lubrication
 - All the above
- The type of lubrication under conditions of slow speed and high load is
 - Thick film or hydrodynamic lubrication
 - Thin film or boundary lubrication
 - High-pressure lubrication
 - All the above
- Limitation of animal and vegetable oils is
 - They have poor oiliness
 - They oxidise to form gummy products
 - They have extremely high-viscosity
 - All the above
- The common antioxidants used to retard the oxidation of lubricating oil is
 - Aromatic phenolic or aminocompounds
 - Alkylated naphthalene's
 - Glycol
 - Tricresylphosphate
- Beside graphite the other commonly used solid lubricants are
 - MoS_2
 - Soapstone
 - Talc
 - All the above
- As temperature increases the viscosity of a lubricating oil
 - Increases
 - Decreases
 - Neither increases nor decreases
 - Either increases or decreases
- Viscosity index of a lubricating oil can be increased by adding organic polymers like
 - Polyisobutylene
 - Phenylenes
 - Amines
 - Ethers
- The property of a lubricant that helps to safeguard against the risk of fire during operation of a machine
 - Viscosity
 - Flash and fire point
 - Cloud and pour point
 - Aniline point
- The suitability of a lubricant in cold conditions is decided by
 - Flash and fire point
 - Steam emulsion number
 - Cloud and pour point
 - Iodine value

11. The parameter that helps in estimating the percentage of aromatics in oil is
 - (a) Aniline point
 - (b) Iodine value
 - (c) Neutralisation number
 - (d) Saponification number
12. The science of friction, lubrication and wear is called
 - (a) Tribology
 - (b) Trichology
 - (c) Surface science
 - (d) Lubrology

Solutions

- | | | | | | | |
|-------|-------|--------|--------|--------|-------|-------|
| 1 (d) | 2 (a) | 3 (b) | 4 (b) | 5 (a) | 6 (d) | 7 (b) |
| 8 (a) | 9 (b) | 10 (c) | 11 (a) | 12 (a) | | |

Chapter 8

PERIODIC PROPERTIES

8.1 Introduction

The genesis of classification of elements dates back to early 1800s when the German chemist Johann Dobereiner made the first attempt to systematise the study of properties of elements and gave the *Dobereiners law of triads*. This was followed by the *Newlands law of octaves*. The first detailed classification of elements was proposed by Russian chemist Dmitri Mendeleev (1837–1907) and German chemist Lothar Meyer (1830–1895). Both these scientists worked independently and in 1869 proposed that when elements are arranged in the increasing order of their atomic weights, similarities appear in their physical and chemical properties at regular intervals. However, the *Mendeleev's periodic table* had certain anomalies, which were addressed in due course of time. Gradual improvement saw the development of the *modern periodic law* (given by Henry Moseley) in which the elements are arranged in the order of increasing atomic numbers.

The elements are arranged in the periodic table in the order of increasing atomic numbers. They are divided into 18 vertical columns called groups and seven horizontal rows termed as periods. According to the IUPAC recommendations, the groups are numbered from 1 to 18, replacing the older notations of groups IA...VIIA, IB...VIIB and zero. The seven periods have 2, 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and will theoretically consist of 32 elements. The properties of the elements vary periodically due to periodic variation in their electronic configuration. In this chapter, we will study the variations in electronic configurations, atomic and ionic sizes, ionisation energies and other related properties.

8.2 Basic Concepts

Before studying the periodicity in properties of elements, it is important to have knowledge of some basic terms and concepts.

- In the atoms, the orbitals are filled in the order of increasing energy (Aufbau principle), that is, an electron will first enter the orbital of lowest energy. The sequence of orbitals in the order of increasing energy is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.

Long Form Of The Periodic Table

Main group elements s-block elements												p-block elements Main group elements																	
1 1.0079 H HYDROGEN 1s												2 4.0026 He HELIUM 1s																	
3 6.941 Li LITHIUM 2s												4 9.012 Be BERYLLIUM 2s																	
11 22.990 Na SODIUM 3s												12 24.305 Mg MAGNESIUM 3s																	
19 39.098 K POTASSIUM 4s												20 40.078 Ca CALCIUM 4s																	
37 85.468 Rb RUBIDIUM 5s												38 87.620 Sr STRONTIUM 5s																	
55 132.91 Cs CAESIUM 6s												56 137.33 Ba BARIUM 6s																	
87 223.02* Fr FRANCIUM 7s												88 226.03* Ra RADIUM 7s																	
11 22.990 Na SODIUM 3s												12 24.305 Mg MAGNESIUM 3s																	
19 39.098 K POTASSIUM 4s												20 40.078 Ca CALCIUM 4s																	
37 85.468 Rb RUBIDIUM 5s												38 87.620 Sr STRONTIUM 5s																	
55 132.91 Cs CAESIUM 6s												56 137.33 Ba BARIUM 6s																	
87 223.02* Fr FRANCIUM 7s												88 226.03* Ra RADIUM 7s																	
21 44.955 Sc SCANDIUM 3d 4s												22 47.902 Ti TITANIUM 3d 4s																	
23 50.942 V VANADIUM 3d 4s												24 51.996 Cr CHROMIUM 3d 4s																	
25 54.938 Mn MANGANESE 3d 4s												26 55.847 Fe IRON 3d 4s																	
27 58.933 Co COBALT 3d 4s												28 58.699 Ni NICKEL 3d 4s																	
29 63.546 Cu COPPER 3d 4s												30 65.70 Zn ZINC 3d 4s																	
31 69.723 Ga GALLIUM 3d 4s 4p												32 72.63 Ge GERMANIUM 3d 4s 4p																	
33 74.922 As ARSENIC 4s 4p												34 78.971 Se SELENIUM 4s 4p																	
35 79.907 Br BROMINE 4s 4p												36 83.801 Kr KRYPTON 4s 4p																	
37 85.468 Rb RUBIDIUM 5s												38 87.620 Sr STRONTIUM 5s																	
39 88.906 Y YTTRIUM 4d 5s												40 91.224 Zr ZIRCONIUM 4d 5s																	
41 92.906 Nb NIOBIUM 4d 5s												42 95.95 Mo MOLYBDENUM 4d 5s																	
43 98.906 Tc TECHNETIUM 4d 5s												44 101.07 Ru RUTHENIUM 4d 5s																	
45 102.91 Rh RHODIUM 4d 5s												46 106.42 Pd PALLADIUM 4d 5s																	
47 107.87 Ag SILVER 4d 5s												48 112.41 Cd CADMIUM 4d 5s																	
49 114.82 In INDIUM 5s 5p												50 118.69 Sn TIN 5s 5p																	
51 121.75 Sb ANTIMONY 5s 5p												52 127.60 Te TELLURUM 5s 5p																	
53 126.90 I IODINE 5s 5p												54 131.29 Xe XEON 5s 5p																	
55 132.91 Cs CAESIUM 6s												56 137.33 Ba BARIUM 6s																	
57 138.91 La LANTHANUM 5d 6s												58 140.12 Ce CERIUM 4f 5d 6s																	
59 140.907* Pr PRASEODYMIUM 4f 5d 6s												60 144.24 Nd NEODYMIUM 4f 5d 6s																	
61 146.92 Pm PROMETHIUM 4f 5d 6s												62 150.35 Sm SAMARIUM 4f 5d 6s																	
63 151.97 Eu EUROPIUM 4f 5d 6s												64 157.25 Gd GADOLINIUM 4f 5d 6s																	
65 158.93 Tb TERBIUM 4f 5d 6s												66 162.50 Dy DYSPROSIUM 4f 5d 6s																	
67 164.93 Ho HOLMIUM 4f 5d 6s												68 167.26 Er ERBIUM 4f 5d 6s																	
69 168.93 Tm THULIUM 4f 5d 6s												70 173.04 Yb YTTERBIUM 4f 5d 6s																	
71 174.97 Lu LUTETIUM 4f 5d 6s												72 178.49 Hf HAFNIUM 5d 6s																	
73 180.95 Ta TANTALUM 5d 6s												74 183.85 W TUNGSTEN 5d 6s																	
75 186.20 Re RHENIUM 5d 6s												76 190.20 Os OSMIUM 5d 6s																	
77 192.22 Ir IRIDIUM 5d 6s												78 195.09 Pt PLATINUM 5d 6s																	
79 196.97 Au GOLD 5d 6s												80 200.59 Hg MERCURY 5d 6s																	
81 204.38 Tl THALLIUM 6s 6p												82 207.19 Pb LEAD 6s 6p																	
83 208.98 Bi BISMUTH 6s 6p												84 209 Po POLONIUM 6s 6p																	
85 209 At ASTATINE 6s 6p												86 209 Rn RADON 6s 6p																	
87 223.02* Fr FRANCIUM 7s												88 226.03* Ra RADIUM 7s																	
89 227.03 Ac ACTINIUM 6d 7s												90 261.11 Rf RUTHERFORDIUM 6d 7s																	
91 262.114 Db DUBNIUM 6d 7s												92 263.118 Sg SEABORGIUM 6d 7s																	
93 262.12 Bh BOHRNIUM 6d 7s												94 265* Hs HASSIUM 6d 7s																	
95 268.14 Mt MEITNERIUM 6d 7s												96 281.16 Ds DARMSTADTIUM 6d 7s																	
97 281.16 Rg ROENTGENIUM 6d 7s												98 281.16 Cn COPERNICIUM 6d 7s																	
99 281.16 Uut UNUNTRIUM 6d 7s												100 281.16 Fl FLEROVIUM 6d 7s																	
101 281.16 Uup UNUNPENTIUM 6d 7s												102 281.16 Lv LIVERMORIUM 6d 7s																	
103 281.16 Uus UNUNSEPTIUM 6d 7s												104 281.16 Uuo UNUNOCTIUM 6d 7s																	
90 261.11 Th THORIUM 5f 6d 7s												91 262.114 Pa PROTACTINIUM 5f 6d 7s																	
92 263.118 U URANIUM 5f 6d 7s												93 262.12 Np NEPTUNIUM 5f 6d 7s																	
94 265* Pu PLUTONIUM 5f 6d 7s												95 268.14 Am AMERICIUM 5f 6d 7s																	
96 281.16 Cm CURIUM 5f 6d 7s												97 281.16 Bk BERKELIUM 5f 6d 7s																	
98 281.16 Cf CALIFORNIUM 5f 6d 7s												99 281.16 Es EINSTEINIUM 5f 6d 7s																	
100 281.16 Fm FERMIUM 5f 6d 7s												101 281.16 Md MEDELEVIUM 5f 6d 7s																	
102 281.16 No NOBELIUM 5f 6d 7s												103 281.16 Lr LAWRENCIUM 5f 6d 7s																	

*Atomic mass of the isotope of longest half life

- The other rules governing the filling of orbitals are
 - *Pauli's exclusion principle*: It was given by Austrian scientist Wolfgang Pauli (1925). It states that in an atom, no two electrons can have the same set of all four quantum numbers. If the principal, azimuthal and magnetic quantum numbers are the same, the electrons will have different spins.
 - *Hund's rule of maximum multiplicity*: It states that electrons in the same subshell (*p*, *d* and *f*) do not pair until all the orbitals of similar energy gain one electron each.
- *Effective nuclear charge*: The hydrogen atom has only one electron, the energy level of which is determined by its principal quantum number *n*. All the orbitals inside this shell have the same energy and the only force experienced by the electron is the attractive force towards the positively charged nucleus. The situation is, however, different in case of multielectron atoms. The electrons in such atoms experience not only attractive force of the nucleus but also repulsion among themselves and each of their neighbours. The repulsion of outer-shell electrons by the inner-shell electrons is particularly important, as the outer shell electrons are pushed away from the nucleus due to repulsion of the inner-shell electrons. As a result, the nuclear charge felt by the outer-shell electrons is less than what it would have been if there were no inner electrons. This net charge felt by the valence electrons is termed as the effective nuclear charge, represented by the symbol (Z_{eff}), and the repulsion experienced due to the inner electrons is the shielding effect. The shielding effect is called so because the inner electrons shield/screen the outer electrons from experiencing the actual nuclear charge ($Z_{\text{eff}} = Z_{\text{actual}} - \text{electron shielding}$).
- Consider the example of fluorine (atomic number = 9); there are two electrons in shell 1 ($n=1$) and seven electrons in shell 2 ($n = 2$). The seven electrons in $n = 2$ will be repelled by two electrons in $n = 1$ hence they will experience less attraction than what they would have experienced in the absence of these two electrons. Hence, these two inner-shell electrons are shielding or screening the outer electrons from the attractive force of the nucleus, and because of this shielding, the effective attractive force felt by the valence electrons reduces. Shielding effect generally remains the same in the period, as in the period the number of shells is the same and it increases down the group.
- *Penetration effect*: It is the tendency of electrons in an orbital to be attracted towards the nucleus. In a multielectron system, penetration is the electron's relative electron density (probability density) near the nucleus and can also be considered as the presence of electrons inside the shell of other electrons. This can be explained by considering the shapes of orbitals and their radial distribution curves (Fig 8.1). The 1s orbital is spherically symmetrical with no node, hence we can see from the curve (Fig 8.1) that it has maximum probability density near the nucleus. On comparing 2s and 2p orbitals, we see that 2s is spherically symmetrical having a sphere within a sphere. It has two regions of high probability separated by a surface of zero probability called the node, and 2p orbital is dumb-bell shaped with electron distribution in identical lobes on either side of the nucleus and separated by a node cutting through the nucleus. This can be seen in Fig 8.1, which shows that 2s penetrates inside 1s (see the small loop of 2s inside 1s orbital in Fig 8.1). The 2p does not penetrate effectively because its wave function goes to zero at the nucleus. Thus 2s is more tightly bound to the nucleus and has lower energy than the 2p orbital. Thus the penetration of 2s is greater than 2p and the electrons in 2s experience large value of Z_{eff} than the electrons in the 2p orbital. For subshells

within the same shell (n), the penetrating power of electron follow the sequence $s > p > d > f$. When the value of shell (n) and subshell (l) are different the penetrating power of electrons follows the trend

$$1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f$$

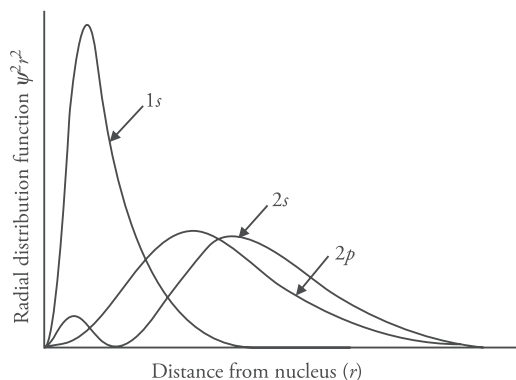


Figure 8.1 Radial distribution function of orbitals

Greater the penetration power of an electron, closer it will be to the nucleus, it will experience greater effective nuclear charge and it will be held firmly. Hence the ionisation enthalpy would be high. Table 8.1 gives the effective nuclear charge of the orbitals of a few atoms.

Table 8.1 Effective nuclear charge Z_{eff} of the orbitals of few atoms

	H							He
Z	1							2
1s	1.00							1.69
	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76
	Na	Mg	Al	Si	P	S	Cl	Ar
Z	11	12	13	14	15	16	17	18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3p			4.07	4.29	4.89	5.48	6.12	6.76

8.3 Periodicity in Properties

Electronic configuration in period: Each period corresponds to the value of n or principal energy level.

First period ($n = 1$) There are only two elements in this period, hence the electronic configuration of the first element hydrogen is $1s^1$ and that of helium is $1s^2$. With this, the first shell or K shell is completely filled.

Second period ($n = 2$) It starts with lithium $1s^2 2s^1$, beryllium with four electrons has the configuration $1s^2 2s^2$. There are eight elements in this period. The configuration of the last element neon is $1s^2 2s^2 2p^6$. The second shell is completely filled.

Third period ($n = 3$) It starts with Na ($1s^2 2s^2 2p^6 3s^1$). This period also has eight elements. The $3s$ and $3p$ orbitals are completely filled; however, the $3d$ orbitals remain vacant as their energy is higher than the energy of $4s$ orbitals. The configuration of the last element [Ar] of this period is $1s^2 2s^2 2p^6 3s^2 3p^6$.

Fourth period ($n = 4$) It starts with potassium, where the electron is added to the $4s$ orbital. The electronic configurations of K and Ca are $[Ar]4s^1$ and $[Ar]4s^2$, respectively. After filling of $4s$ orbital, the filling of $3d$ orbital becomes energetically favourable. It starts at Sc ($Z = 21$), which has the configuration $[Ar]3d^1 4s^2$ and ends at Zn ($Z = 30$) with electronic configuration $[Ar]3d^{10} 4s^2$. There are certain irregularities in filling of $3d$ orbitals, for example, Cr ($Z = 24$) and Cu ($Z = 29$) have the electronic configuration $[Ar]3d^5 4s^1$ and $[Ar]3d^{10} 4s^1$, respectively, against the expected configuration of $[Ar]3d^4 4s^2$ and $[Ar]3d^9 4s^2$, respectively. These ten elements from Sc to Zn constitute the *first transition series*. Filling of $4p$ orbital starts at Ga ($Z = 31$) and is completed at Kr ($Z = 36$).

Fifth period ($n = 5$) It begins with rubidium ($Z = 37$) where the next electron enters the $5s$ orbital and this orbital is complete at Sr ($Z = 38$). After this, ten electrons fill the $4d$ shell Y ($Z = 39$) to Cd ($Z = 48$), where the valence shell configurations are $4d^1 5s^2$ and $4d^{10} 5s^2$, respectively. This is termed as the *second transition series*. However, molybdenum has the configuration $4d^5 5s^1$ and Ag has the configuration $4d^{10} 5s^1$. The filling of $5p$ orbitals begins at In ($Z = 49$) and is completed at Xe ($Z = 54$).

Sixth period ($n=6$) It contains 32 elements. The orbitals are filled in the order $6s$, $4f$, $5d$ and $6p$. The filling of $4f$ orbitals begins with cerium ($Z = 58$) and ends with lutetium ($Z = 71$) to give the $4f$ -inner transition series termed as the *lanthanoid series*.

Seventh period ($n = 7$) The filling of orbitals is similar to the sixth period with successive filling of $7s$, $5f$, $6d$ and $7p$ orbitals. The filling of $5f$ orbitals starts with Th ($Z = 90$) and is completed at Lw ($Z = 103$). This series from Th to Lw is called the $5f$ -inner transition series or the *actinoid series*. The $4f$ and $5f$ inner transition series are placed separately below the periodic table to comply with the principle of placing elements with similar properties in a single column.

Table 8.2 gives the IUPAC-recommended names for some groups and sections in the periodic table.

Table 8.2 IUPAC-recommended names of some groups and sections

Group number	IUPAC-recommended name
1 (except H)	Alkali metals
2	Alkaline earth metals
15	Pnictogens
16	Chalcogens
17	Halogens
18	Noble gases
1(except H), 2, 13, 14, 15, 16, 17, 18	Main group elements

8.4 Types of Elements on the Basis of Their Electronic Configuration

Depending on the orbital in which the last electron enters, elements are classified in to four blocks, viz s-block, p-block, d-block and f-block elements.

1. *s-block elements*: They are elements of groups 1 (alkali metals) and 2 (alkaline earth metals) in which the valence electrons enter the s-orbitals. Their outer electronic configuration is ns^1 and ns^2 , respectively. They are soft metals with low melting and boiling points, reactive as they have low ionisation enthalpies and strong reducing agents as they lose electrons readily to acquire stable noble gas configuration. Their common oxidation states are +1 and +2, respectively. Their reactivity increases down the group and most of them form ionic compounds, with the exception of lithium and beryllium.
2. *p-block elements*: They are elements of groups 13 to 18, in which the valence electron enters the p-orbitals. Their outermost electronic configuration varies from ns^2np^1 to ns^2np^6 . The *p-block elements* together with *s-block elements* are termed as the *representative elements* or the *main group elements*. The p-block elements include both metals and nonmetals. The nonmetallic character increases as we move from left to right across the period and the metallic character increases as we move from top to bottom in the group. Their ionisation enthalpies are higher than that of s block elements. The elements of group 18 (noble gases) with electronic configuration ns^2np^6 are very stable because of completely filled valence electrons. They have very low chemical reactivity. Elements of group 17 (halogens) with electronic configuration ns^2np^5 and group 16 (chalcogens) with electronic configuration ns^2np^4 have highly negative electron gain enthalpies (earlier termed as electron affinity) and they gain one and two electrons, respectively, to acquire the stable noble gas configuration. Some of these elements exhibit more than one oxidation state.
3. *d-block elements*: They are elements of group 3 to 12, in which the last electron enters the d-orbitals of their second last (penultimate) energy level. Their outer electronic configuration is $(n-1) d^{1-10}ns^{0-2}$. These elements are mostly metals, have high melting and boiling points, generally form coloured complexes, exhibit variable valency (oxidation states) and exhibit paramagnetism, and many elements like Mn, Ni, Co, Cr, V and Pt and their compounds are used as catalysts. These are termed as transition elements as they act as a bridge between highly reactive elements of groups 1 and 2 and less reactive elements of groups 13 and 14. The d block consists of the following:

First transition series (4th period where 3d orbital is filled), Sc (Z=21) to Zn (Z=30)

Second transition series (5th period where 4d orbitals is gradually filled) Yttrium (Z=39) to Cd (Z=48)

Third transition series (6th period where 5d orbitals are gradually filled) Lanthanum (Z=57), Hafnium (Z=72) and mercury (Z=80)

Fourth transition series (7th period where 6d orbitals are gradually filled) – It is incomplete series.

4. *f-block elements*: *f*-block elements comprises of two rows of elements placed at the bottom of the periodic table. In these elements, the last electron enters the *f*-orbital. However, the last electron is added to the third to the outermost (antepenultimate) energy level; $(n-2)f$, hence these elements are termed as inner transition element. These elements are characterised by the general electronic configuration $(n-2) f^{1-14}(n-1)d^{0\text{or}1}ns^2$
 - (a) The first series called *lanthanoid series* extends from Ce(Z=58) to Lu(Z=71). They are also termed as rare earth elements and have the general electronic configuration is $4f^{1-14}5d^{0\text{or}1}6s^2$.
 - (b) The second series of elements from Th(Z=90) – Lr(Z=103) is called the *actinoid series*; their general electronic configuration is $5f^{1-14}(n-1)d^{0\text{or}1}7s^2$

All the *f* block elements are metals having high melting and boiling points. They exhibit variable oxidation state and form coloured ions. These elements also have the tendency to form complex compounds. Actinoid elements exhibit radioactivity. They have been prepared in nanogram quantities by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called trans-uranium elements.

Note: IUPAC recommends the use of the terms lanthanoids and actinoids over lanthanides and actinide, as ‘ide’ usually implies negatively charged ions. However, the terms lanthanides and actinides are still commonly used.

8.5 Periodic Trends in Properties of Elements

The physical and chemical properties of elements vary periodically. This has been attributed to similarity in the outer electronic configuration after regular intervals. Let us discuss the periodic trends of some important properties:

Atomic and Ionic Radii

Atomic radius is the distance from the centre of the nucleus to the outermost shell of the electrons. Since it is difficult to obtain an isolated atom, and the electron cloud around an atom does not have a sharp boundary, it is not possible to obtain the atomic radii by direct measurement for an individual atom. For a nonmetal, atomic radius is considered half the distance between the nuclei of two similar atoms bonded together by a single covalent bond (covalent radius) and for a metal it is half the distance between centres of nearest neighbours in a metallic crystal (metallic radius). Both metallic and covalent radii are jointly referred to as the atomic radii. (Table 8.3). For example the inter-nuclear distance between Cl–Cl is 198 pm, hence its atomic radius is taken as $198/2 =$

99 pm and the distance between two adjacent copper atoms in solid copper is 256 pm, hence its metallic radius would be $256/2 = 128$ pm

$$r_{\text{covalent}} = \frac{\text{Inter-nuclear distance between two similar bonded atoms}}{2}$$

Noble gases do not form covalent bonds, hence their atomic radius is found out by calculating their van der Waals radius, which is defined as half the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules. This can be explained by considering the example of two chlorine molecules in close contact (Fig 8.2)

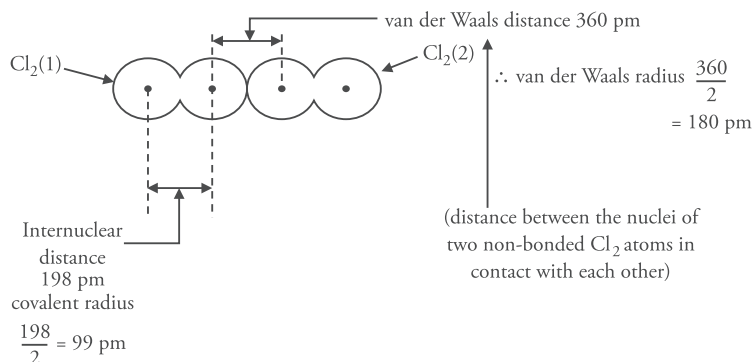


Figure 8.2 Depiction of van der Waals radii

Atomic radius can be found by X-ray diffraction, electron diffraction and other spectroscopic techniques.

Trends in atomic and ionic radii: Table 8.3 and Figure 8.3 show the atomic radii of some elements in the period and group, respectively. It is observed that the atomic radii increases down the group and decreases from left to right across the period within s and p block. The atomic radius increases down the group because as one moves down the group the valence electrons occupy the orbitals of successively higher principal quantum number. The valence electrons in Li, Na, K, Rb, Cs, Fr occupy second ($2s^1$), third ($3s^1$), fourth ($4s^1$), fifth ($5s^1$), sixth ($6s^1$), and seventh ($7s^1$), shells, respectively. Since larger shells are occupied, hence the atomic size increases down the group.

The atomic radius decreases across the period, because the valence electrons in a period occupy the same shell but the nuclear charge increases progressively thereby increasing the effective nuclear charge on the valence electrons drawing them closer to the nucleus and decreasing the atomic radii (Fig 8.3). However, it is observed that the atomic radius of second and third rows of d-block elements are almost similar. This is due to lanthanide contraction. The elements of the third row of d block elements (sixth period) are preceded by 14 lanthanoids where 4f orbitals are occupied. Since these orbitals have poor shielding properties, the valence electrons experience greater attraction towards the nucleus. The repulsions between electrons fails to compensate for the increasing nuclear charge, so Z_{eff} increases from left to right, resulting in the decrease in atomic radii, and the sizes of elements of second and third rows of d-block elements remain almost the same.

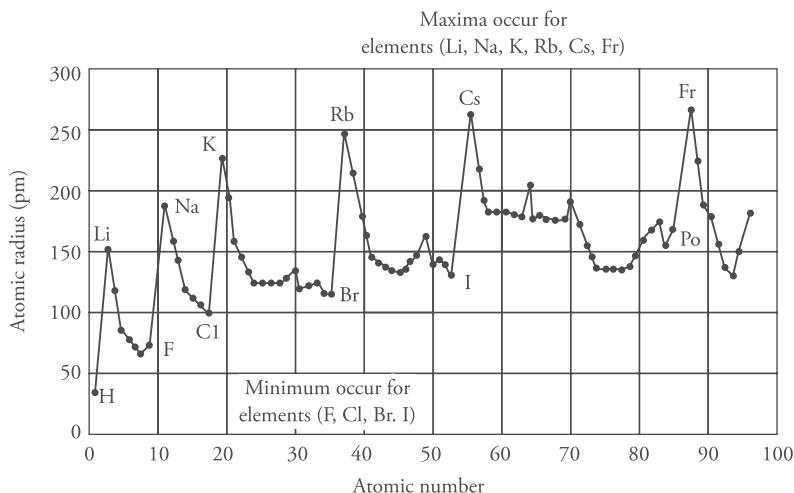


Figure 8.3 Trends in atomic radius and atomic number

Table 8.3 Atomic radii of elements in pm

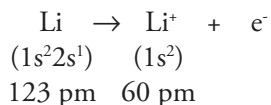
Radius increases																		Radius decreases																	
↓																		→																	
H 37																		He																	
Li 152		Be 112																B 83		C 77		N 75		O 73		F 72		Ne* 160							
Na 186		Mg 160																Al 143		Si 117		P 110		S 104		Cl 99		Ar* 191							
K 227		Ca 197		Sc 162		Ti 147		V 134		Cr 128		Mn 127		Fe 126		Co 125		Ni 124		Cu 128		Zn 134		Ga 135		Ge 122		As 120		Se 116		Br 114		Kr	
Rb		Sr 215		Y 180		Zr 160		Nb 146		Mo 139		Tc 136		Ru 134		Rh 134		Pd 137		Ag 144		Cd 151		In 167		Sn 140		Sb 140		Te 143		I 133		Xe	
Cs 248		Ba 222		La 187		Hf 159		Ta 146		W 139		Re 137		Os 135		Ir 136		Pt 138		Au 144		Hg 151		Tl 170		Pb 175		Bi 150		Po 167		At		Rn	

*The radii of noble gases are van der Waals radii

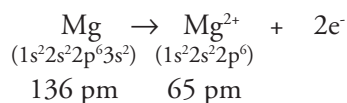
Increase in nuclear charge: It results in greater attraction of the orbital electrons towards the nucleus thereby decreasing the atomic radius. As noticed in the Table 8.3, the radius of Ne and Ar is large. This is because it represents the van der Waals radius. The atomic radius increase down the group because while descending in a group two things happen: (i) increase in nuclear charge and (ii) addition of new shells. The second factor outweighs the first, leading to increase in atomic radius from top to bottom.

Variation in ionic radii: It has been observed that the radius of cation (positive ion) is always smaller than that of the parent atom and the radius of anion (negative ion) is always larger than that of the parent atom.

The size of cation decreases not only due to the increase of effective nuclear charge Z_{eff} due to loss of valence electrons thereby decreasing electron–electron repulsions but also due to the fact that generally formation of cation leads to the complete loss of the valence shell. For example the configuration of Li is $1s^2 2s^1$ and that of Li ion is $1s^2$. Here the 2s shell is completely lost.



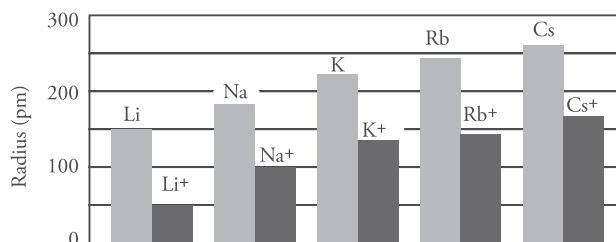
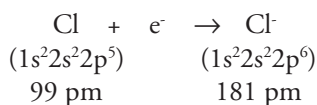
Similarly, formation of Mg^{2+} ion (formed by the complete loss of 3s shell) is represented as follows:



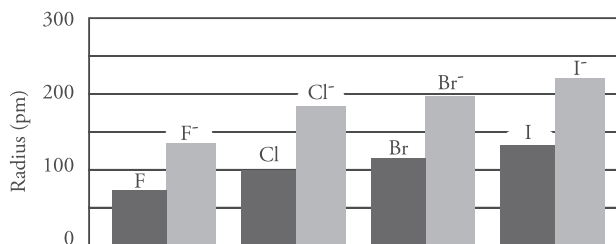
The radius of cation increases down the group

Size of anion increases because addition of electron increases inter-electronic repulsion in the orbital electrons, and hence the electron cloud expands leading to the increase in size. This is also associated with the decrease in Z_{eff}

For example,



(a) Radius of cation is smaller than the parent atom



(b) Radius of anion is larger than the parent atom

Figure 8.4 (a) and (b) Comparison of atomic and ionic radii of cations (group 1) and anions (group 17)

Trends in ionic radii: Like atomic radii, the ionic radii also increases down the group and decreases across the period. However, there are some exceptions to this trend.

8.6 Ionisation Enthalpy

First ionisation energy is defined as the energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state at 0 K.



The second ionisation energy is the energy required to remove the most loosely bound electron from the resulting cation.



Energy required to convert $A^{2+}(g)$ in to $A^{3+}(g)$ is the third ionisation energy and so on. Ionisation energies are expressed in kJ mol^{-1} or electronvolts (eV), where $1 \text{ eV} = 94.485 \text{ kJ mol}^{-1}$.

However, most chemical reactions occur at constant pressure and at a temperature of 298 K. In such a situation it is more appropriate to use the term ionisation enthalpy. If the gaseous atoms are assumed to be ideal gases then the ionisation enthalpy is larger than ionisation energy by $\frac{5}{2}R\Delta T$,

where R is the molar gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$) and ΔT is the difference between the two temperatures (0 K and 298 K). The ionisation energies for the removal electrons are of the order of 10^3 kJ mol^{-1} and the ionisation enthalpy is

$$\Delta H(298K) = \Delta H(0K) + \frac{5}{2} \times 8.314 \times 10^{-3} \times 298$$

$$\Delta H(298K) = \Delta H(0K) + 6.2 \text{ kJ mol}^{-1}$$

The difference between ionisation energy and enthalpy is very small ($\approx 6 \text{ kJ mol}^{-1}$) and is often ignored. However, the term ionisation enthalpy is commonly used these days.

The ionisation energy depends upon the size of the atom, charge on the nucleus, type of electrons involved (s, p, d, f) on the screening effect of the inner electrons and the penetration effect of electrons. The ionisation enthalpies of elements with $Z=1$ to 60 are shown in Fig 8.5. From the figure it is clear that alkali metals have low ionisation enthalpies and noble gases have very high ionisation enthalpies. This can be attributed to the fact the alkali metals have only one electron in their valence shell. All the inner shell electrons called core electrons shield this electron from the nucleus thereby reducing Z_{eff} , hence they lose electrons easily and acquire a stable noble gas configuration. Noble gases because of stable electronic configuration do not lose electrons readily, which is reflected in their very high values of ionisation enthalpies.

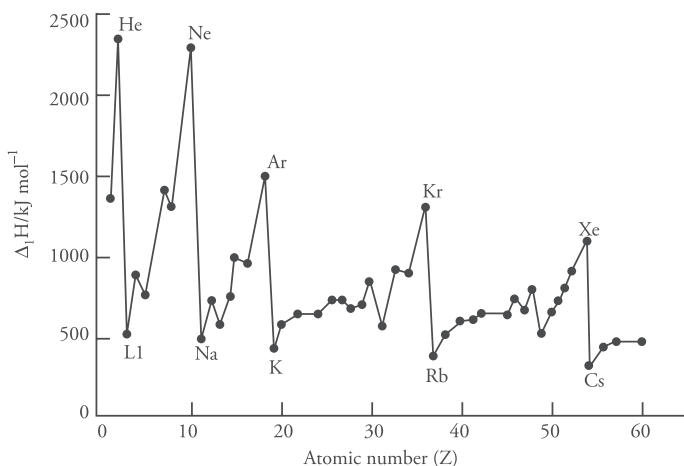


Figure 8.5 Variation of first ionisation enthalpies ($\Delta_i H$) with atomic number for elements with $Z = 1$ to 60

Variation in a group

The ionisation enthalpy decreases as we descend down the group. On moving down the group, the following factors become effective:

- Nuclear charge increases.
- New shells are added.
- The shielding of outermost electrons increases due to increase in the number of inner electrons.

The first factor is outweighed by the second and third factors, as a result of which the ionisation enthalpy decreases on descending down the group. Fig 8.6(b) shows the variation of ionisation enthalpy of the elements of group 1. Table 8.4 gives the first and second ionisation enthalpies of elements.

Variation in a period

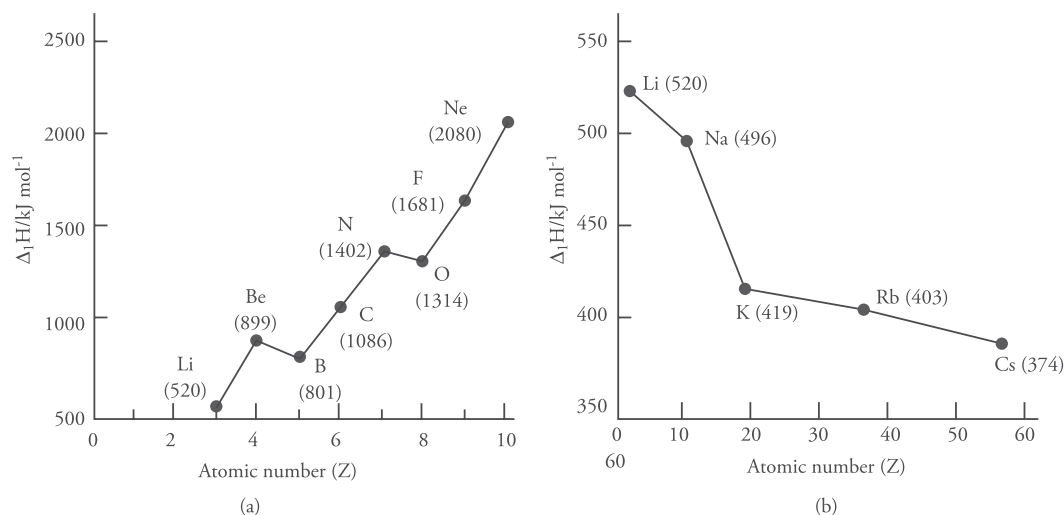
In a period the ionisation enthalpy generally increases from left to right. This is because nuclear charge increases in a period and the successive electrons are added in the orbitals with same principal quantum level resulting in the increase in Z_{eff} . Consequently the electrons are more tightly held by the nucleus, resulting in an increase in ionisation enthalpy. Figure 8.6(a) shows the variation of ionisation enthalpy of the elements of the second period.

However, there are some deviations in this general trend. Although the nuclear charge of B is greater than Be, the first ionisation enthalpy of B ($Z=5$) is slightly less than Be ($Z=4$). This is because of the fact that in beryllium the electron is removed from s orbital, whereas in boron the electron is removed from p orbital. Since the penetration of 2s electron to the nucleus is more than that of 2p electron, it is easier to remove electron from 2p orbital, and hence the ionisation enthalpy of boron is less than that of Be.

Similarly O ($Z=8$) has lesser ionisation enthalpy than N ($Z=7$). This is because nitrogen has half-filled 2p orbitals which reside in different atomic orbitals whereas in oxygen, two of the four 2p orbitals reside in the same orbital thereby increasing the electron–electron repulsion. Hence it is easier to remove the 2p electron of oxygen. Moreover, the half-filled p orbitals of nitrogen is a stable configuration.

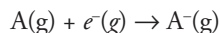
Table 8.4 First and second ionisation enthalpies of elements in kJ mol^{-1}

H 1312							He 2373 5259
Li 520 7297	Be 899 1757	B 801 2426	C 1086 2352	N 1402 2855	O 1314 3386	F 1681 3375	Ne 2080 3952
Na 495 4562	Mg 737 1476	Al 577 1816	Si 786 1577	P 1011 1903	S 1000 2251	Cl 1251 2296	Ar 1520 2665
K 419 3051	Ca 589 1145	Ga 579 1979	Ge 762 1537	As 947 1798	Se 941 2044	Br 1139 2103	Kr 1351 3314
Rb 403 2632	Sr 549 1064	In 558 1821	Sn 708 1412	Sb 834 1794	Te 869 1795	I 1008 1846	Xe 1170 2045
Cs 374 2420	Ba 502 965	Tl 590 1971	Pb 716 1450	Bi 704 1610	Po 812 1800	At 926 1600	Rn 1036

**Figure 8.6** (a) First ionisation enthalpies ($\Delta I H$) of elements of the second period as a function of atomic number (Z) and (b) $\Delta I H$ of alkali metals as a function of Z .

8.7 Electron Gain Enthalpy

Electron gain enthalpy is defined as the energy change when an electron is added to an isolated gaseous atom in ground state to give an anion represented by the equation



$$\Delta_{EG} = E(A^-, g) - E(A, g)$$

Δ_{EG} is the electron gain enthalpy.

If the energy is released during the addition of an electron, then the electron gain enthalpy is considered negative and if energy is supplied to add electron to the atom, then the electron gain enthalpy is considered as positive. The electron gain enthalpy is measured in kJ mol^{-1} or electronvolts (eV). Table 8.5 gives the electron gain enthalpies for few atoms.

Electron affinity E_a on the other hand is the difference in energy between the gaseous atoms and the gaseous ions at $T = 0$

$$E_a = E(A, g) - E(A^-, g)$$

Hence the sign convention of electron gain enthalpy and electron affinity are opposite $\Delta_{EG} = -E_a$

Note that the sign convention for electron affinity is the reverse of the convention used in thermodynamics. A positive value of electron affinity indicates that the ion A^- has a lower energy than the atom A . Although the term electron affinity is widely used in inorganic chemistry, the terms electron gain enthalpy and electron affinity cannot be used interchangeably. In the present text, we shall use the term electron gain enthalpy.

Table 8.5 Electron gain enthalpies (kJ mol^{-1}) of some elements

H -72							He +48
Li -60	Be ≈ 0	B -27	C -122	N ≈ 0	O -141 +780	F -328	Ne +116
Na -53	Mg ≈ 0	Al -43	Si -134	P -72	S -200 +492	Cl -349	Ar +96
K -48	Ca ≈ 0	Ga -29	Ge -116	As -78	Se -195	Br -325	Kr +96
Rb -47	Sr ≈ 0	In -29	Sn -116	Sb -103	Te -190	I -295	Xe +77

*The second value given for sulphur and oxygen is for the addition of second electron to the anion

From Table 8.5, it is clear that the electron gain enthalpy increases in a period and decreases down the group. This is because as one moves from left to right in the period the effective nuclear charge increases hence an electron is easily added. Elements of group 17 add electron easily to acquire a stable noble gas configuration; hence they have high negative electron gain enthalpy. Electron gain enthalpy decreases down the group, because on moving down, the group the atomic radius increases and the added electron feels lesser attraction by the nucleus, that is, Z_{eff} decreases.

However, the electron gain enthalpy of S and Cl is larger than O and F. This is because the elements of second period are relatively smaller in size than the elements of the third period. In the second period, the electrons are added in the second shell ($n=2$), where because of small size, the incoming electron feels greater interelectronic repulsion in the relatively compact 2p subshell. In the third period, because of larger size, the inter-electronic repulsion is less and hence, electron is added easily with the release of energy.

Noble gases have a stable electronic configuration, hence energy has to be supplied to add electron to them, and this is reflected by their high positive values of electron gain enthalpy.

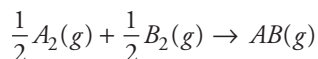
Successive electron gain enthalpies: Except noble gases, the first electron gain enthalpy of most elements is negative. However, the second electron gain enthalpy is positive for all elements, since energy is to be supplied to force the second electron into the anion. Table 8.5 gives the electron gain enthalpies for a few elements.

8.8 Electronegativity

Electronegativity χ (chi) is defined as the ability of a bonded atom to attract the shared pair of electron towards itself.

Consider the formation of a covalent bond between two similar atoms of a molecule like hydrogen. In this case the electron pair participating in bond formation is shared equally by both the atoms, but this is not the case when a covalent bond is formed between two dissimilar atoms, like HCl. In this case, chlorine exerts greater attraction on the electron pair; consequently the electron pair lies closer to the Cl atom. Hence we can say that Cl has greater electronegativity than H. Since the electron pair lies closer to Cl, it develops partial negative charge (δ^-) and the hydrogen atom develops partial positive charge (δ^+) and the covalent bond thus acquires ionic character.

Several scales like Pauling scale, Mulliken–Jaffe scale and Allred–Rochow scale have been developed to express the electronegativity of elements numerically. The most widely accepted among these is the Pauling scale developed by the American scientist Linus Pauling. He computed the values of electronegativity by making use of the concepts related to the energetics of bond formation. For example, consider the formation of AB from diatomic molecules A_2 and B_2



The bond energy for AB is

$$E_{AB} = \frac{1}{2}[E_{AA} + E_{BB}] + \Delta_{AB}$$

where E_{AA} and E_{BB} are the bond energies of purely covalent molecules A_2 and B_2 , respectively. The bond between A and B is stronger than if the bond was purely covalent; hence Δ_{AB} accounts for this extrastability. Pauling gave a relation to express stability of the bond to the tendency of atoms to attract electrons.

$$\Delta_{AB} = 96.48(\chi_A - \chi_B)^2$$

where χ_A and χ_B are the electronegativities of atoms A and B, respectively. The value of Δ_{AB} in the above equation is expressed in kJ mol^{-1} . If it is expressed in kcal mol^{-1} as done originally by Pauling, the equation becomes

$$\Delta_{AB} = 23.06(\chi_A - \chi_B)^2$$

Pauling arbitrarily assigned a value of 4.0 to fluorine, the most electronegative element in the periodic table.

Robert Mulliken observed that if an atom has high ionisation enthalpy, it means that high energy is required to remove that electron, which in turn means that the electron is tightly bound to the nucleus. Similarly an atom with high electron affinity also has high attraction towards an electron. On the basis of the above arguments, Mulliken proposed that atoms with high ionisation enthalpy and high electron affinity have high electronegativity. He expressed electronegativity as the average value of ionisation enthalpy and electron affinity (both expressed in electronvolts).

$$\chi_M = \frac{1}{2}(I + E_a) \text{ where } \chi_M \text{ is the electronegativity on Mulliken scale.}$$

The Allred and Rochow electronegativity scale is based on the electrostatic attraction between the valence shell electrons and the nucleus. They proposed the equation

$$\chi_{AR} = \frac{35.9Z_{\text{eff}}}{r^2} + 0.744$$

where χ_{AR} is electronegativity on Allred Rochow scale, r is the covalent radius in picometers and Z_{eff} is the effective nuclear charge.

According to Allred Rochow scale elements with high Z_{eff} and small covalent radius will have high electronegativity, and these elements lie close to fluorine.

However, Pauling scale is used throughout the chapter.

Table 8.6 Electronegativity values (on Pauling scale) of elements across the periodic table

H 2.1							
Li 1.0	Be 1.5		B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc..... Zn 1.3.....1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y..... Cd 1.2.....1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La..... Hg 1.1.....1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	As 2.1

Table 8.6 shows that the electronegativity values increase from left to right and decrease down the group. This is because across the period, Z_{eff} increases and hence the nucleus is more likely to attract electron. Similarly down the group, atomic size and Z_{eff} decreases thereby reducing the ability of the nucleus to attract electrons towards itself. Consequently the electronegativity decreases on moving down the group.

Applications of electronegativity

1. *Nature of bond:* The difference in electronegativity of the two bonding atoms helps in predicting the nature of the bond. The bond between A and B will be a non-polar covalent bond if $\chi_A = \chi_B$ and it will have some ionic character if $\chi_A \neq \chi_B$. If $\chi_A > \chi_B$ then the form A^-B^+ will be stable and if $\chi_A < \chi_B$ then A^+B^- will be stable. Greater the difference $\chi_A - \chi_B$ greater will be the ionic character in the bond. Pauling predicted the % ionic character on the basis of electronegativity difference of atoms A and B . He calculated that when

$\chi_A - \chi_B = 1.7$, the bond is approximately 50% ionic and 50% covalent. When

$\chi_A - \chi_B > 1.7$, then the ionic character will be greater than 50%. Bonds having more than 50% ionic character are termed as ionic bonds and those which are more than 50% covalent are termed as covalent bonds. However, Paulings, results did not hold good when (i) $\chi_A - \chi_B$ values are too large and (ii) Alkali metal hydrides and hydrides of Ca , Sr and Ba are ionic although the value of $\chi_M - \chi_H$ is less than 1.7.

Hanny and Smith revised the Pauling equation and gave a new equation for the calculation of % ionic character

$$\begin{aligned}\% \text{ ionic character} &= 100 \times [0.16(\chi_A - \chi_B) + 0.035(\chi_A - \chi_B)^2] \\ &= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2\end{aligned}$$

The above equation shows that a bond AB is 50% ionic if $\chi_A - \chi_B = 2.1$. On substituting the electronegativity values of H , F , Cl , Br and I in Hanny and Smith's equation, the % ionic character in HF , HBr , HCl and HI molecules is 43%, 17%, 13% and 7%, respectively. Thus the percentage ionic character decreases in the order $\text{HF} > \text{HBr} > \text{HCl} > \text{HI}$.

2. *Stability and strength of a bond:* Greater the difference in χ_A and χ_B , greater is the stability of the bond. For example, the stability of hydrogen halides decreases in the order $\text{HF} > \text{HBr} > \text{HCl} > \text{HI}$ as shown below

$$\chi_{\text{F}} = 4.0 \quad \chi_{\text{Cl}} = 3.0 \quad \chi_{\text{Br}} = 2.8 \quad \chi_{\text{I}} = 2.5 \quad \chi_{\text{H}} = 2.1$$

$$H - X \text{ bond } H - F \quad H - Cl \quad H - Br \quad H - I$$

$$\chi_X - \chi_H \quad 1.9 \quad > \quad 0.9 \quad > \quad 0.7 \quad > \quad 0.4$$

($X = \text{F, Cl, Br, I}$)

Stability of compounds in which $\chi_A - \chi_B$ is very small: Such compounds in which

$\chi_A - \chi_B$ is very small tend to be unstable. Examples of such compounds are SiH_4 , NCl_3 , PH_3 , AsH_3 , SbH_3 and BiH_3 , where $\chi_A - \chi_B$ values are 0.3, 0.0, 0.0, 0.1, 0.2 and 0.2, respectively.

Stability of compounds in which $\chi_A - \chi_B$ is very large: These compounds are generally formed by the combination of metals (whose χ values are very low) and non metals (whose χ values are very large). In such case, $\chi_A - \chi_B$ will be large and these compounds will be stable with large heats of formation, high melting and boiling points.

3. *Acid–base character of normal oxides of elements in a period:* On moving from left to right in a period the acidic character of oxides increases. On moving across the period the electronegativity of the elements increases consequently the difference in electronegativity of element and oxygen $\chi_E - \chi_O$ decreases. This is illustrated in Table 8.7, considering the oxides of elements of the third period.

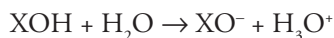
Table 8.7 Electronegativity difference and nature of oxides

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
χ_E	0.9	1.2	1.5	1.8	2.1	2.5	3.0
$\chi_O - \chi_E$ $\chi_O = 3.5$	2.6	2.3	2.0	1.7	1.4	1.0	0.5
Acid/base character	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	Very strongly acidic

4. *Metallic and non-metallic character of elements:* The electronegativity values increase from left to right across the period and decrease from top to bottom down the group. Consequently metallic character of elements decreases across the period and increases down the group. Elements on the left of periodic table are metallic in nature and those on the right of the periodic are non-metals.

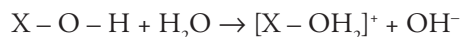
The increase in the metallic character down the group is very pronounced in groups 14 and 15, which begin with non-metals (C and N) and end with metals (Pb and Bi).

5. *Acidic and basic character of XOH molecule:* When XOH ionises in aqueous solution (X may be a metal or a non-metal) two case may arise
 - (i) When $\chi_O - \chi_X < \chi_O - \chi_H$, the polarity of OH bond is more than the polarity of X–O bond, consequently the XOH molecule will ionise in aqueous solution as shown below



Since H_3O^+ ions are produced, XOH behaves as an acid.

- (ii) When $\chi_{\text{O}} - \chi_{\text{X}} > \chi_{\text{O}} - \chi_{\text{H}}$, the polarity of the bond XO is more than the polarity of O–H bond and hence ionisation will occur as follows



\therefore XOH molecule gives OH^- ions hence it behaves as a base.

Thus we find that the electronegativity concept helps in predicting the acidic or basic nature of XOH compounds.

Gallais suggested that if χ_{X} is greater than 1.7, the compound XOH is acidic and if it is lesser than 1.7, the compound XOH shows basic character.

6. *Colour of salts*: Colour of salts is closely related to the percentage ionic character. The relation of ionic character of a bond and colour of a compound has been generalised as given in Table 8.8.

Table 8.8 Variation of colour of compound with % ionic character

S. No	% ionic character	Colour of compound
1.	Less than 20%	Coloured
2.	Greater than 20%	Colourless
3.	Lesser and lesser than 20%	Colour goes on deepening

Example: AgCl (white: 80% ionic character); AgBr (pale yellow: 24% ionic character); AgI (yellow: 15% ionic character); Ag₂S (black: 4% ionic character)

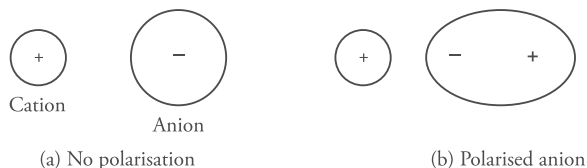
7. *Calculation of bond length*: If two atoms A and B with different electronegativities are bonded together then the bond length of AB is given by the formula

$$d_{\text{A-B}} = r_{\text{A}} + r_{\text{B}} - 0.09(\chi_{\text{A}} - \chi_{\text{B}})$$

where r_{A} and r_{B} are the covalent radii of A and B, respectively, and $\chi_{\text{A}} - \chi_{\text{B}}$ is the electronegativity difference. The normal bond length between A and B would be $r_{\text{A}} + r_{\text{B}}$, but the difference in electronegativity reduces the bond length by the factor $0.09(\chi_{\text{A}} - \chi_{\text{B}})$.

8.9 Polarising Power and Polarisability: Fajan's Rule

When a cation approaches an anion, the positive charge of the cation attracts the electrons of the anion and repels the positively charged nucleus of the anion. As a result of these two effects, the anion is no longer symmetrical but is bulged towards the cation. This is called distortion, deformation or polarisation of the anion and the ability of the cation to polarise the anion is termed as its polarisation power. The anion also exerts a similar effect on the cation, but since the size of cation is less, the effect is less pronounced.

**Figure 8.7** Polarisation of anion by cation

Greater polarisation implies greater covalent character as the electrons will be drawn from the negative ion towards the positive ion resulting in high concentration of electrons between the two nuclei. Fajan put forward rules summarising the factors that favour polarisation and hence covalency.

- (i) *Charge on cation or anion:* The polarising power of the cation increases with an increase in positive charge. This is because a cation with higher charge can attract electron effectively. For example, in NaCl , MgCl_2 and AlCl_3 , the charge on cation is Na^+ , Mg^{2+} and Al^{3+} , respectively; thus the polarising power of cation increases from Na^+ to Al^{3+} and hence the covalent character of their chlorides increases from NaCl to AlCl_3 .

Similarly polarisability of anion increases with the increase in negative charge, because with the increase in negative charge the anion will be able to repel its outermost electrons more effectively.

- (ii) *Size of cation or anion:* Small cation causes greater polarisation of anion due to concentration of positive charge, in small area. The polarising power of Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and Ra^{2+} follows the order $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Ra}^{2+}$, because their cation radii increases in the reverse order. On the other hand, large anion is polarised easily, because the effective nuclear charge on outer electrons is less. Example – consider halides of Ca like CaF_2 , CaCl_2 , CaBr_2 , CaI_2 . Their covalent character increases in order $\text{CaF}_2 < \text{CaCl}_2 < \text{CaBr}_2 < \text{CaI}_2$, which is reflected by the decrease in melting point ($\text{CaF}_2 = 1392^\circ\text{C}$, $\text{CaCl}_2 = 772^\circ\text{C}$, $\text{CaBr}_2 = 730^\circ\text{C}$ and $\text{CaI}_2 = 575^\circ\text{C}$).

- (iii) *Electronic configuration of cation:* Cations with noble gas configuration have less polarising power. Polarisation and hence covalency is favoured by cation having non-inert gas configuration ($ns^2p^6d^{10}$). Thus Cu^+ (18 electron structure) causes greater polarisation of Cl^- ion than Na^+ (8 electron structure) in spite of having the same charge and nearly the same size. Hence compounds of Cu^+ are more covalent than compounds of Na^+ .

Fajan's rule is helpful in predicting the covalent character of compounds in a group and in a period. In a group, the charge on cation remains the same but its size increases hence the tendency to form covalent bond decreases down the group. In a period, the electronic charge increases and size decreases; hence the covalent character increases across the period. However, indiscriminate application of the concept of polarisation may lead to wrong predictions. Other factors should also be considered, for example considering the chlorides of sodium, potassium and rubidium; on the basis of polarisation concept their covalent character should decrease from NaCl to KCl to RbCl , but their melting points are in the order $\text{NaCl} = 800^\circ\text{C}$, $\text{KCl} = 776^\circ\text{C}$ and $\text{RbCl} = 715^\circ\text{C}$. Thus RbCl is more covalent. This is because other physical parameters like lattice energy also play an important role in deciding the ionic or covalent character of a compound.

8.10 Oxidation State

The trends in oxidation states can be understood by considering the electronic configuration, ionisation energies, electron affinities, completely and half-filled valence shells. Elements gain or lose electrons to acquire a stable configuration. The common trends in oxidation states of elements are discussed below:

Main group elements

The oxidation state of main group elements generally depends upon the electronic configuration. It is generally equal to the number of electrons in the outermost shell or eight minus the number of electrons in the outermost shell.

Table 8.9 Oxidation state of the main group elements:

Group	1	2	13	14	15	16	17	18
Number of valence electrons	1	2	3	4	5	6	7	8
Oxidation state	1	2	3	4	3, 5	2, 6	1, 7	0, 8

The electronic configuration of groups 1 and 2 is [noble gas] ns^1 and [noble gas] ns^2 , respectively, where n represents the valence shell. Hence they lose one and two electrons, respectively, to acquire the stable noble gas configuration. All elements of group I (Li, Na, K, Rb, Cs, Fr) exhibit oxidation state +1 and elements of group II (Be, Mg, Ca, Sr, Ba, Ra) exhibit oxidation state +2.

Group 13 (Boron family): They have three valence electrons, two in s -subshell and one in p -subshell. Therefore, they show a maximum oxidation state +3. However, except boron other elements show +1 oxidation state also and in the last element thallium +1 oxidation state is more stable than +3 oxidation state. This effect in which the stable oxidation number of an element is two less than the oxidation number of the group is termed as the *inert pair effect*. This effect can be explained on the basis ionisation enthalpies and bond energies. Table 8.10 gives the ionisation energies and bond energies of elements of group 13.

Table 8.10 Ionisation energies and bond enthalpies of group 13 elements

Element	First ionisation enthalpy I_1 kJ/mol	$I_1 + I_2 + I_3$ kJ/mol	Avg M-Cl bond energy kJ/mol
B	801	6828	536
Al	578	5139	494
Ga	579	5521	481
In	558	5083	439
Tl	589	5439	373

It is clear from Table 8.10 that the ionisation energy increases from Al to Ga and In to Tl which is contrary to the normal trend. This is because of poor shielding of outer shell electrons by electrons in the d and f orbitals thereby increasing Z_{eff} making it very difficult to remove the ns^2 electrons. Another factor contributing to inert pair effect is the decrease in bond energy down the group. The net result of these two effects is that large amount of energy is required to remove two ns^2 electrons (due to high ionisation enthalpy) but less energy is released during bond formation (low bond energy). Hence oxidation number of an element is two less than the oxidation number of the group (inert pair effect).

Group 14 (Carbon family): The common oxidation state is +4; however, due to inert pair effect Ge, Sn and Pb also show +2 oxidation state. In lead compounds +2 oxidation state is more stable than +4 oxidation state.

Group 15 (Nitrogen family): They have five electrons in their valence shell. It is difficult to lose five electrons due to energy considerations, hence they gain three electrons to complete their octet. Common oxidation state is -3; however, they exhibit +3 and +5 oxidation state also. Nitrogen exhibits oxidation state from -3 to +5 in its hydrates, oxides and oxoacids.

Group 16 (Oxygen family): Common oxidation state of oxygen is +2; however, the oxidation state of oxygen in OF_2 and H_2O_2 is +2 and -1, respectively. Apart from +2 oxidation state other elements like sulphur exhibit higher oxidation states like +4 and +6 due to availability of vacant d orbitals.

Group 17 (Halogen family): The most common oxidation state of the elements of this group is -1. However, due to presence of vacant d orbitals elements (Cl, Br, I) show higher oxidation state like +3, +5 and +7 also. Fluorine, the first member of this group is the most electronegative element in the periodic table.

Group 18 (Noble gases): Although inert, they exhibit oxidation states +2, +4, +6 and +8

Transition elements: Transition metals show variable oxidation states. Table 8.11 gives the oxidation state of elements of the first transition series.

Table 8.11 Oxidation state of elements of the first transition series

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic configuration	d^1s^2	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2	$d^{10}s^1$	$d^{10}s^2$
Oxidation state	+2 +3	+2 +3 +4	+2 +3 +4 +5	+1 +2 +3 +4 +5 +6	+2 +3 +4 +5 +6 +7	+2 +3 +4 +5 +6	+2 +3 +4 +5	+2 +3 +4	+1 +2 +3	+2

Lanthanoids: The most common oxidation state is +3; however, some elements exhibit +2 and +4 oxidation state to acquire the stable noble gas configuration. Example: Cerium gives Ce^{4+} ($4f^0$), europium and terbium gives Eu^{2+} and Tb^{4+} ($4f^7$) and ytterbium forms Yb^{2+} ($4f^{14}$). Few other elements also exhibit +2 and +4 oxidation states.

Actinoids: All actinoids have an oxidation state of +3; however, this is not always the most stable oxidation state.

Summary

- The elements are arranged in the periodic table in the order of increasing atomic number. The electrons occupy the atomic orbitals in the order of increasing energy in the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p and 7s.
- Effective nuclear charge is the net attractive force experienced by valence electrons, ($Z_{\text{eff}} = Z_{\text{actual}} - \text{shielding}$). Shielding effect is the reduction in effective nuclear charge due to repulsion felt by valence electrons due to the presence of electrons in the inner shell.
- Penetration effect is the tendency of electrons to be attracted towards the nucleus. Within the same shell (n) the penetration power of electrons follows the sequence $s > p > d > f$.
- Each period in the periodic table corresponds to the value of n or principal energy level in which the electrons enter into s, p, d and f block elements; the last electrons enter the s, p, d and f orbitals, respectively.
- The atomic and ionic radii decreases in a period and increases down the group. The radii of noble gases is large as it represents the van der Waals radius.
- Ionisation enthalpy is the energy required to remove the most loosely bound electron from an isolated gaseous atom. Its value increases in a period and decreases down the group.
- Electron gain enthalpy is defined as the energy change when an electron is added to an isolated gaseous atom in ground state. Generally energy is released during addition of electron (hence electron gain enthalpy is negative) but in noble gases energy is to be supplied to add electron (positive electron gain enthalpy). Addition of second electron to an anion requires energy, hence second electron gain enthalpy is positive.
- Electronegativity is the ability of a bonded atom to attract the shared electron pair towards itself. It leads to development of ionic character in a bond. It is measured on various scales, the most popular being the Pauling scale in which fluorine, the most electronegative element has been assigned a value of 4.0
- Fajans rule describes polarising power and polarisability. A small cation with high charge and non – inert gas configuration has greater tendency to polarise an anion. A large anion with increase in negative charge have greater polarisability. Greater the polarisation, greater is the ionic character.
- Oxidation state of an element depends upon its electronic configuration. Common oxidation state for various group as:
Group I = +1. Group II = +2, Group 13 = +3; Group 14 = 4; Group 15 = 3, 5;
Group 16 = 2, 6; Group 17 = 1, 7; Group 18 = 0, 8.

- Metals show variable oxidation states. The most common oxidation state of lanthanoids is +3, although some elements show +2 and +4 oxidation state also. The most common oxidation state of actinoids is +3 although it is not always stable.

Review Questions

- Write the general outer electronic configuration of s, p, d and f block elements. Explain the general properties of elements belonging to these groups.
- Explain the terms effective nuclear charge, shielding and penetration effect.
- Differentiate between atomic radius, ionic radius and van der Waals radius. How does atomic radius vary in a group and in a period.
- Explain why the size of cation is less and that of anion is more than the corresponding atom.
- What do you understand by the isoelectronic species. Explain the variation in the size of isoelectronic species.
- Define ionisation enthalpy. In the second period explain why the ionisation enthalpies follow the order $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F} < \text{Ne}$.
Explain why ionisation enthalpy of Be is higher than B and ionisation enthalpy of oxygen is lower than nitrogen and fluorine.
- How does ionisation enthalpy vary in a period and in a group. Explain why the first ionisation enthalpy of sodium is lower than that of magnesium but its second ionisation enthalpy is higher than that of magnesium.
- What is electron gain enthalpy and electron affinity. What is the difference between the two. Except noble gases the first electron gain enthalpy for most elements is negative but the second electron gain enthalpy is positive. Explain with the help of suitable example.
- What is the difference between the terms electron gain enthalpy and electronegativity. Explain the periodic trends of electronegativity in the periodic table.
- State and explain the Fajan's rule.

Multiple Choice Questions

- Which of the following elements will have the outer electronic configuration $(n-1)d^5ns^1$
 - Cr
 - Cu
 - Ar
 - Na
- The number of protons in an element with general electronic configuration of the ultimate and penultimate shell as $(n-1)s^2(n-1)p^6(n-1)d^xns^2$, where $n = 4$ and $x = 5$ will be
 - 26
 - 22
 - 25
 - 28

3. In the following sets of elements the atomic radii will increase in the order
 - (a) Mg, K, Na, Rb
 - (b) Mg, Na, K, Rb
 - (c) Na, K, Rb, Mg
 - (d) Na, Rb, K, Mg
4. The correct order for the second ionisation enthalpy of C, N, O and F is
 - (a) $C > N > O > F$
 - (b) $O > N > F > C$
 - (c) $O > F > N > C$
 - (d) $F > O > N > C$
5. The outer electronic configuration of the most electronegative element is
 - (a) ns^2np^3
 - (b) ns^2np^4
 - (c) ns^2np^5
 - (d) ns^2np^6
6. The atom having maximum electron gain enthalpy is
 - (a) F
 - (b) Cl
 - (c) Br
 - (d) I
7. The electronegativity of the following elements increase in the order
 - (a) C, N, Si, P
 - (b) N, Si, C, P
 - (c) P, Si, N, C
 - (d) Si, P, C, N
8. Consider the cations Cr^+ , Cr^{2+} , Cr^{3+} , Cr^{4+} and Cr^{6+} and the anions F^- , Cl^- , Br^- and I^- . Which of the above cation has greatest polarising power and which of the anions has maximum polarisability
 - (a) Cr^{6+} , F^-
 - (b) Cr^{2+} , Cl^-
 - (c) Cr^+ , I^-
 - (d) Cr^{6+} , I^-
9. The decreasing order of solubility of silver halide is
 - (a) $AgI > AgBr > AgCl > AgF$
 - (b) $AgF > AgCl > AgBr > AgI$
 - (c) $AgCl > AgF > AgBr > AgI$
 - (d) $AgBr > AgF > AgI > AgCl$
10. Which of the following bonds has maximum polarity
 - (a) C – O
 - (b) C – F
 - (c) C – S
 - (d) C – Br
11. The % ionic character of a bond between two atoms is calculated from the difference between their
 - (a) Electronegativities
 - (b) Electron affinities
 - (c) Ionisation energies
 - (d) Ionic radii
12. Which among the following has the largest size
 - (a) Br^-
 - (b) I
 - (c) I^-
 - (d) I^+

Solution

- | | | | | | | | |
|-------|--------|--------|--------|-------|-------|-------|-------|
| 1 (a) | 2 (c) | 3 (b) | 4 (c) | 5 (c) | 6 (b) | 7 (d) | 8 (d) |
| 9 (b) | 10 (b) | 11 (a) | 12 (c) | | | | |

Chapter 9

ACID–BASE, OXIDATION–REDUCTION AND INTERMOLECULAR FORCES

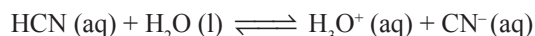
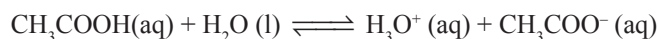
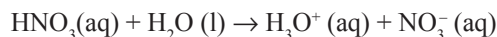
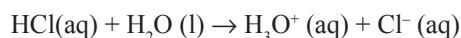
9.1 Introduction

Different investigators have put forward different concepts to characterize acid and base. This chapter deals with the various concepts of acids and bases that have developed over the years. Some of the important concepts of acid and base are discussed below:

9.2 Arrhenius Concept

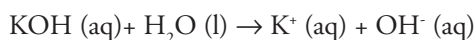
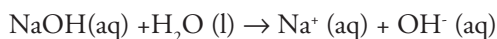
According to Arrhenius concept given in 1884, an acid is a substance that dissociates to give hydrogen ion when dissolved in water and a base is a substance that dissolves in water to give hydroxyl ions.

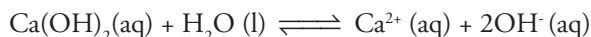
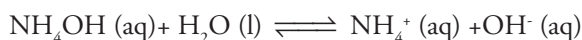
HCl, HNO₃, CH₃COOH and HCN are acids because they ionise in water to liberate H⁺ ions.



The H⁺ ions furnished by the acid are solvated and exist as H₃O⁺ ions in solution. The solvated proton is known as the *hydronium* ion, referred to as the *oxonium* ion in older literature.

Likewise, NaOH, KOH, NH₄OH and Ca(OH)₂ are bases because they ionise in water to liberate OH⁻ ion.





Note: In the above equations, H_2O represents the solvent.

According to Arrhenius concept, acids like HCl and H_2SO_4 that ionise almost completely in aqueous solutions are strong acids and CH_3COOH and HCN that are weakly ionised are termed as weak acids. Similarly, bases like NaOH and KOH which ionise completely to give OH^- ions are strong bases and Ca(OH)_2 and Al(OH)_3 which are partially ionised in water are termed as weak bases.

Neutralisation reaction may be expressed as

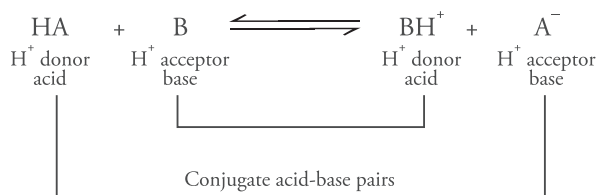


Due to its simplicity, Arrhenius concept was widely accepted; however, its major limitation is that it can be applied only to aqueous solutions and fails to account for the acid–base behavior in solvents other than water, that is, non –aqueous solvents. Arrhenius concept fails to account for basicity of substances like NH_3 that do not contain OH group.

9.3 Bronsted–Lowry Concept

J.N Bronsted and T.M Lowry in 1923 independently arrived at the definition of acid and base that do not always involve water. According to the Bronsted–Lowry concept, an acid is capable of donating protons and a base is capable of accepting protons. In other words, acid is a proton donor and a base is a proton acceptor.

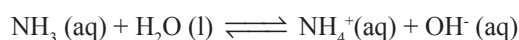
Consider the following general reaction:



In the above reaction, HA donates a proton (hence a Bronsted–Lowry acid) to give A^- , which can accept a proton in the reverse reaction (hence A^- acts as a Bronsted–Lowry base). Similarly, B is a proton acceptor (Bronsted–Lowry base), which on accepting a proton form BH^+ , which is a proton donor in the reverse reaction (Bronsted–Lowry acid).

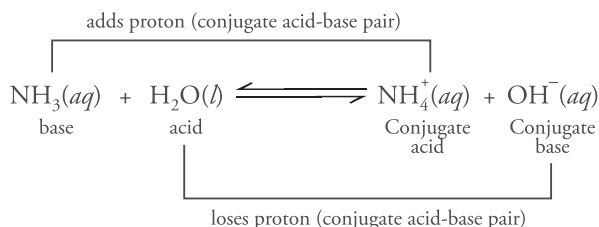
Thus we see that the Bronsted–Lowry acid and base donate and accept protons, respectively, to give product that themselves act as acid and base. Such chemical species which differ by a proton are termed as conjugate acid base pairs. Hence A^- is a conjugate base of the acid HA and HA is a conjugate acid of base A^- . Similarly, B is a conjugate base of acid BH^+ and BH^+ is a conjugate acid of the base B .

Consider ionisation of NH_3 in water, which may be represented as



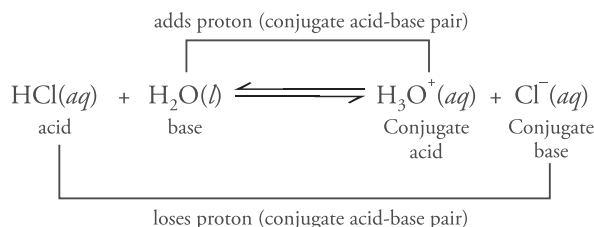
In the above reaction, water molecule acts as a proton donor, and hence it is called Lowry–Bronsted acid, whereas ammonia molecule accepts a proton and hence it is the Lowry–Bronsted base. In the reverse reaction, ammonium ion (NH_4^+) donates a proton and hence it acts as an acid and OH^- accepts a proton and is therefore a base.

Water is a conjugate acid of hydroxyl ion and hydroxyl ion is a conjugate base of water molecule. Similarly ammonia is a conjugate base of ammonium ion and ammonium ion is a conjugate acid of NH_3 molecule. This may be expressed as



It may be noted here that if Bronsted acid is a strong acid, then its conjugate base is a weak base and vice versa.

Similarly, the ionisation of HCl in water may be represented as

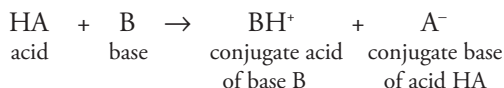


In the above reaction, HCl donates a proton (acid) to give Cl^- (its conjugate base). Similarly H_2O acts as a base and accepts a proton to form its conjugate acid H_3O^+ .

Thus we see that H_2O has a dual role, it acts as an acid (proton donor) in the presence of NH_3 and it acts as base (proton acceptor) in the presence of HCl . Such substances are said to be amphiprotic.

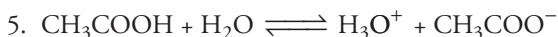
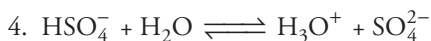
Strength of Bronsted acids

A general prototype equation for an acid–base reaction can be written as

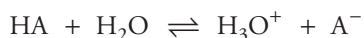


To explain the strength of acids, let us consider the following series of reactions.

1. $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
2. $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_4^-$
3. $\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$



In the reactions 1, 2 and 3, HCl , H_2SO_4 and HNO_3 undergo complete ionisation in water and they exist as solvated proton known as the hydronium ion. All three have the same conjugate acid species (H_3O^+) but have different conjugate bases (Cl^- , HSO_4^- , NO_3^- respectively). Such acids are termed as *strong acids* or more correctly strong acids in water. The ionisations 4, 5 do not proceed to completion (hence the equilibrium sign), the conjugate acid H_3O^+ is not completely formed hence these are *weak acids*. The strength of acid is measured by the position of equilibrium. For example, for a weak acid in water



The equilibrium constant is given by

$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

For dilute solutions, $[\text{H}_2\text{O}]$ is virtually constant hence

$$K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

K_a is known as the acid dissociation constant and is a measure of the strength of acid in a particular solvent which should be specified. Since K_a is proportional to H_3O^+ it implies that K_a values for strong acid is large and for weak acids the value of K_a is small. However, it is a common practice to express the values as negative logarithm to the base 10, that is, $-\log_{10} K_a$ written as pK_a . Therefore, $pK_a = -\log_{10} K_a$.

Table 9.1 gives the pK_a values for acids in aqueous solutions.

Table 9.1 pK_a values of some acids in aqueous solution at 298 K

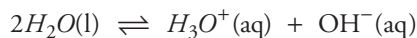
Acid	HA	A ⁻	K _a	pK _a	Acid	HA	A ⁻	K _a	pK _a
Hydroiodic	HI	I ⁻	10 ¹¹	-11	Formic	HCOOH	HCO ₂ ⁻	1.8 × 10 ⁻⁴	3.75
Perchloric	HClO ₄	ClO ₄ ⁻	10 ¹⁰	-10	Ethanoic	CH ₃ COOH	CH ₃ CO ₂ ⁻	1.74 × 10 ⁻⁵	4.76
Hydrobromic	HBr	Br ⁻	10 ⁹	-9	Carbonic	H ₂ CO ₃	HCO ₃ ⁻	4.3 × 10 ⁻⁷	6.37
Hydrochloric	HCl	Cl ⁻	10 ⁷	-7	Ammonium ion	NH ₄ ⁺	NH ₃	5.6 × 10 ⁻¹⁰	9.25
Sulphuric	H ₂ SO ₄	HSO ₄ ⁻	10 ²	-2	Hydrocyanic	HCN	CN ⁻	4.9 × 10 ⁻¹⁰	9.31
Nitric	HNO ₃	NO ₃ ⁻	10 ²	-2	Hydrofluoric	HF	F ⁻	3.5 × 10 ⁻⁴	3.45
Hydronium ion	H ₃ O ⁺	H ₂ O	1	0	Hydrogen sulphide	H ₂ S	HS ⁻	9.1 × 10 ⁻⁸	7.04
Phosphoric	H ₃ PO ₄	H ₂ PO ₄ ⁻	7.5 × 10 ⁻³	2.12	Sulphurous	H ₂ SO ₃	HSO ₃ ⁻	1.5 × 10 ⁻²	1.81

Similarly the proton transfer equilibrium for a base is expressed as the base dissociation constant K_b .



$$K_b = \frac{[HB^+][OH^-]}{[B]} \text{ and } pK_b = -\log_{10} K_b$$

Water being amphiprotic undergoes autoprotolysis or autoionisation where proton transfer occurs from one water molecule to the other.



Equilibrium constant is given by

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

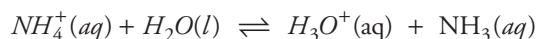
$$K[H_2O]^2 = [H_3O^+][OH^-]$$

Since water is feebly ionised, the product $K[H_2O]^2$ may be considered as constant and is represented by K_w .

$$K_w = [H_3O^+][OH^-]$$

K_w is the ionic product of water or the autoionisation or autoprotolysis constant of water and its value at 25 °C is 1.00×10^{-14} indicating that only a very tiny fraction of water molecules are present as ions in pure water. In pure water $[H_3O^+] = [OH^-] = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$, hence the pH of pure water is 7.

The autoionisation constant helps to express the strength of base in terms of the strength of its conjugate acid. Consider the reaction

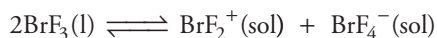


The value of K_b for equilibrium where NH_3 acts as a base is related to the value of K_a where its conjugate acid acts as an acid by the relation $K_a K_b = K_w$. This shows that K_a and K_b are inversely related to each other, that is, a strong base has a weak conjugate acid and vice versa.

Like acidity and basicity constant it is convenient to report K_w as its common logarithm (logarithm to the base 10). Hence $K_a K_b = K_w$ can be written as $pK_w = pK_a + pK_b$.

9.4 The Solvent System Definition of Acids and Bases

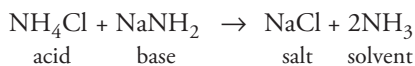
Cady and Elsey extended the Bronsted–Lowry definition of acids and bases to species that do not include proton transfer. Many solvents undergo autoionisation to give positive and negative ions like water.



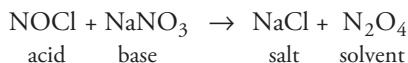
Here 'sol' denotes solution of the non ionised species. In the solvent system any solute that increases the concentration of positive ions characteristic of the solvent (solvo-cations) for example H_3O^+ in case of H_2O , NH_4^+ in liquid NH_3 and NO^+ in N_2O_4 is termed as an acid and substances that increase the concentration of negative ions characteristic of the solvent (solvo-anions for example OH^- in case of H_2O , NH_2^- in liquid NH_3 and NO_3^- in N_2O_4) is termed as a base.

The above definition can be illustrated with the help of the following example.

NH_4Cl is an acid and NaNH_2 is a base as they furnish NH_4^+ and NH_2^- ions respectively. The neutralisation reaction is as follows:



Similarly



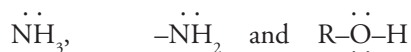
NOCl is an acid as it furnishes NO^+ ions and NaNO_3 is a base as it furnishes NO_3^- ions.

9.5 Lewis Concept of Acid and Base

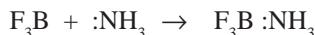
In 1923, American scientist G.N. Lewis proposed a very general and broad based definition of acid and bases. He defined base as an electron pair donor and acid as an electron pair acceptor. The bond formed between a Lewis base and Lewis acid is essentially a coordinate bond.

The definition of Lewis base covers the following substances:

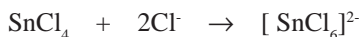
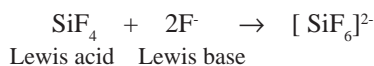
- Neutral species having at least one lone pair of electrons eg. ammonia, amines and alcohols.



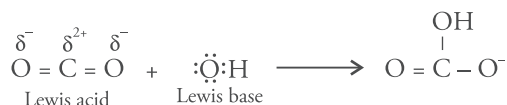
- Negatively charged species or anions like chloride (Cl^-), cyanide (CN^-), hydroxide (OH^-) etc. All the species having vacant orbitals and can accept a lone pair of electron act as Lewis acid. The following substances fall in this category.
- All cations are regarded as Lewis acid as they can accept an electron pair. Large cations like Na^+ , K^+ and Ca^{2+} ions have very little tendency to accept electrons; hence they are weak acids whereas smaller cations like H^+ , Ag^+ and Fe^{2+} have greater tendency to accept electrons, hence they behave as strong acids.
- Electron-deficient compounds in which the central atoms can expand their valence shell. The central atom in compounds like BF_3 , BCl_3 and AlCl_3 have only six electrons around them; hence they have a tendency to accept electrons to complete their octets.



- Molecules in which the central atoms have vacant d orbitals and can extend their valency beyond the octet, for example, SnCl_4 , SiF_4 and SiF_5 the central atoms have vacant d orbitals.



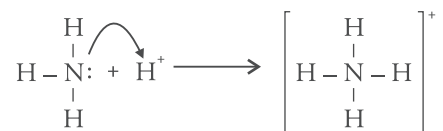
- Molecules in which atoms of different electronegativities are joined by multiple bonds. For example the carbon atom in CO_2 behaves as a Lewis acid because oxygen atom being more electronegative than carbon pulls the electrons towards itself making the carbon atom electron deficient. Hence it can accept an electron pair.



Similarly, the S atom in SO_2 and SO_3 also acts as a Lewis acid.

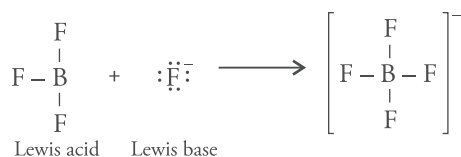
Acid–base reaction according to Lewis theory is as follows:

- Reaction between H^+ ion and NH_3

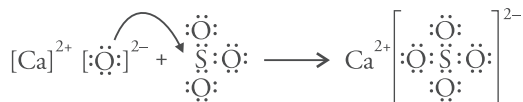


In the above reaction ammonia acts as an electron pair donor (Lewis base) and the proton acts as an electron acceptor (Lewis acid).

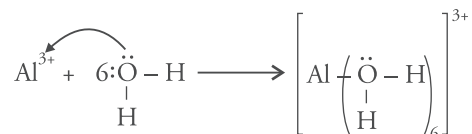
- Reaction between BF_3 and F^-



- Combination of CaO and SO_3



4. Hydration of a metal ion



The Lewis concept has some limitations also.

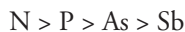
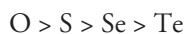
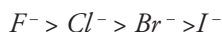
1. It is too general and includes all reactants that can form coordinate bonds. Metals in zero oxidation state like Fe, Ni, Co and Mn are also termed as lewis acids in their complexes with pi acceptor ligands like CO, cyclopentadiene and olefins.
2. Lewis concept fails to explain the relative strength of acid and bases.
3. All chemical reactions involve transfer of electrons; hence all types of reactions become acid–base reactions according to lewis system.

9.6 Hard Soft Acids and Bases

Ahrland, Chatt and Davies in 1958 classified metals and ligands into two classes.

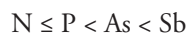
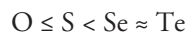
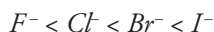
Class a metals: These constitute ions of alkali and alkaline earth metals, lighter metals in higher oxidation states like Ti^{4+} , Cr^{3+} , Fe^{3+} and Co^{3+} and hydrogen ion H^+ . They are characterised by small size, high polarising power, high oxidation state and their outer electrons or orbitals are not easily distorted.

Class a ligands: These ligands combine preferentially with metal ions of ‘class a’. For example ligands NH_3 , R_3N , H_2O and F^- have great tendency to coordinate with ‘class a’ metal ions. The tendency of ligands to form complexes with metals of ‘class a’ is in the order



Class b metals: These include ions of heavier transition metals and those in lower oxidation states having large size and their outer electrons or orbitals are easily distorted.

Class b ligands: These are ligands that combine preferentially with metal ions of ‘class b’. Ligands such as R_3P (phosphines) and R_2S have great tendency to coordinate with ‘class b’ metal ions. The tendency of complexation of ligands with ‘class b’ metal ions follows the order



R.G. Pearson (1963) introduced the terms hard and soft for ‘class a and b’, respectively. In his classification, metal ions of ‘class a’ are called hard acids and ligands of ‘class a’ are called hard bases and on the other hand the metals and ligands of ‘class b’ are termed as soft acids and bases, respectively.

Soft bases have donor atoms that are easily polarised, have low electronegativity and are easy to oxidise.

Hard bases have donor atoms that have low polarisability, high electronegativity and are hard to oxidise.

Soft acids are those in which the acceptor atoms are large in size, have low positive charge and contain unshared pair of electrons (*p* or *d*) in valence shell, that is, they have high polarisability and low electronegativity and do not have noble gas configuration.

Hard acids are those in which the acceptor atoms are small in size, have high electronegativity, low polarisability and have a noble gas configuration.

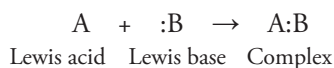
However it is important to note that there is no sharp line of demarcation between soft and hard species and a number of borderline cases also exist.

HSAB principle: This principle states that hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases. It is important to understand that the principle refers to only hard–hard and soft–soft interactions. It has no relation with the strength. Also the principle does not state that hard–soft or soft–hard interactions do not exist. However given a choice hard–hard or soft–soft interactions are preferred over soft–hard interactions.

The bonding in hard acids and bases is electrostatic and can be explained in terms of ionic or dipole–dipole interactions, whereas bonding in soft acids and bases is covalent and are explained in the basis of polarisation.

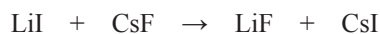
Applications of HSAB principle

1. *Stability of complexes:* Consider the reaction



On the basis of HSAB principle, the complex AB will be stable if both A and B are either hard acids and bases or soft acids and bases. For example, AgI_2^- is stable but AgF_2^- does not exist. This is because, Ag^+ is a soft acid, F^- is a hard base and I^- is a soft base. Therefore AgI_2^- (soft acid + soft base) is a stable complex. Similarly, CoF_6^{3-} (hard acid + hard base) is more stable than CoI_6^{3-} (hard acid + soft base).

2. *Predicting feasibility of a reaction:* The reaction given can be explained using the HSAB principle



In the above reaction, soft iodide prefers to combine with soft caesium ion and hard fluoride combines with hard lithium ion.

3. For *heterogenous catalysis*, HSAB principle says that soft metals adsorb soft bases and for solubility the rule is that hard solute dissolves in hard solvents and soft solutes dissolves in soft solvents.
4. *Occurrence of minerals:* Hard acids such as Ca^{2+} , Mg^{2+} and Al^{3+} appear as CaCO_3 , MgCO_3 and Al_2O_3 , respectively, as the anions CO_3^{2-} and O^{2-} are also hard. These cations are never found as sulphides as S^{2-} as it is a soft base. On the other hand, soft acids like Cu^{2+} , Ag^+ and Hg^{2+}

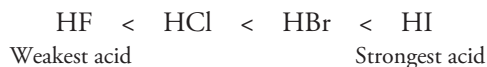
combine with soft base S^{2-} and exist as sulphides. The intermediate acids such as Ni^{2+} , Pb^{2+} and Cu^{2+} are found both as sulphides and carbonates. The combination of hard acids and hard bases mainly occurs through ionic bonding as in $Mg(OH)_2$ and that of soft acids and soft bases occur mainly through covalent bonding as in HgI_2^- .

Table 9.2 Hard Soft acids and bases

Hard	Borderline case (i.e., intermediate)	Soft
Acids H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Mn^{2+} , Co^{3+} , Cr^{2+} , Cr^{3+} , Al^{3+} , Fe^{3+} , Ti^{4+} , Si^{4+} , Zr^{4+} , La^{3+} , Lu^{3+} , Ce^{3+} , Sn^{4+} SO_3 , BF_3 .	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Sn^{2+} , Sb^{3+} , Rh^{3+} SO_2 , BBr_3 , GaH_3	Cu^+ , Au^+ , Ag^+ , Tl^+ , Hg_2^{2+} , Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+} BH_3 , $GaCl_3$, $InCl_3$, I^+ , Br^+ , I_2 , Br_2
Bases H_2O , OH^- , F^- , CH_3COO^- , PO_4^{3-} , SCN^- SO_4^{2-} , Cl^- , CO_3^{2-} , ClO_4^- , NO_3^- ROH , RO^- , R_2O , NH_3 , RNH_2 , N_2H_4	$C_6H_5NH_2$, C_5H_5N , Br^- NO_2^- , SO_3^{2-} , N_2	R_2S , RSH , RS^- , I^- , SCN^- $S_2O_3^{2-}$, R_3P , R_3As , $(RO)_3P$, CN^- , RNC , CO , C_2H_4 , C_6H_6 , H^-

*The underlined element represents the bonding site

- Relative stabilities of compounds:* Table 9.2 helps in predicting the relative stabilities of compounds and complexes. For example, AgI_2^- is stable but AgF_2^- does not exist. This is because, Ag^+ is a soft acid, F^- is a hard base and I^- is a soft base. Therefore, AgI_2^- (soft acid + soft base) is a stable complex. Similarly CoF_6^{3-} (hard acid + hard base) is more stable than CoI_6^{3-} (hard acid + soft base).
- Predicting relative strength of halogen acids in aqueous medium:* HF is the weakest acid as both H^+ and F^- are hard acid and hard base hence HF is stable and does not dissociate easily in aqueous solution. HI (hard acid and soft base) being unstable dissociates easily and hence is a strong acid. The relative strength of acids is



The HSAB concept although useful gives only a qualitative idea and does not offer any quantitative scale of measurement. For example, both OH^- and F^- are hard bases but the former is 10^{13} times stronger base than the latter. The HSAB concept fails to explain this difference of base strength.

- Prediction of donor atom in ambidentate ligand:* If a ligand has two donor atoms, one of which is a hard base and the other is a soft base then the hard base forms complex with hard acid and the soft base forms complex with soft acid. For example $[SCN]^-$ is an ambidentate ligand where N is a hard base and S is a soft acid. Therefore, the ligand coordinates through N atom to form $[Co(NCS)_4]^{2-}$ (both Co and N are hard) and through S atom to form $[Pd(SCN)_4]^{2-}$ as both Pd and S are soft.

9.7 Solubility Equilibria

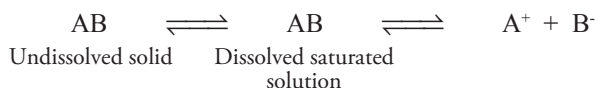
We are well aware of the fact that salts like NaCl dissolve completely in water and said to be soluble, whereas salts like lithium fluoride do not dissolve in water and are termed as insoluble. The solubility of a salt in water depends upon its lattice energy and solvation energy of the ions in solution.

Lattice energy is a measure of attractive forces between the ions in a crystal lattice. It is also the energy to be provided to break the crystal lattice. *Solvation energy* is the energy released when the ions interact with the solvent molecules. A compound will dissolve in a solvent if the solvation energy is greater than the lattice energy. If the solvation enthalpy is small and is not sufficient to overcome the lattice energy then the compound will be insoluble in the solvent.

We shall now discuss the equilibrium between a sparingly soluble salt and its saturated aqueous solution.

Solubility product constant or solubility product:

A saturated solution of sparingly soluble binary electrolyte AB such as BaSO_4 , AgCl and PbS has two simultaneous equilibrium.



The equilibrium constant is given by the equation

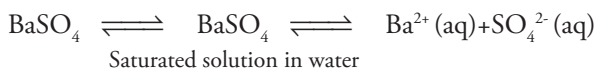
$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}$$

In a saturated solution the concentration of AB is regarded as constant at a given temperature. Hence

$$\begin{aligned} K[\text{AB}] &= [\text{A}^+][\text{B}^-] \\ \text{or } K_{\text{sp}} &= [\text{A}^+][\text{B}^-] \end{aligned}$$

$K_{\text{sp}} = K[\text{AB}]$ is the solubility product constant or simply solubility product. For a binary electrolyte, it is defined as the product of ionic concentration (expressed in mol/liter) in its saturated solution at a given temperature.

Consider the following example:



$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

K_{sp} is an experimental quantity and is not affected by the presence of other ions in solution so long as the solution is very dilute. Table 9.3 gives the K_{sp} values for some sparingly soluble salts

Table 9.3 K_{sp} values for some sparingly soluble salts at 298 K

Salt	Formula	K_{sp} (298 K)
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Calcium carbonate	$CaCO_3$	4.9×10^{-9}
Calcium hydroxide	$Ca(OH)_2$	4.7×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.1×10^{-33}
Copper (I) chloride	$CuCl$	1.7×10^{-7}
Copper (I) sulfide	Cu_2S	2.3×10^{-48}
Copper (II) sulfide	CuS	6.0×10^{-37}
Iron (II) hydroxide	$Fe(OH)_2$	4.9×10^{-17}
Iron (II) sulfide	FeS	6.0×10^{-19}
Iron (III) hydroxide	$Fe(OH)_3$	2.6×10^{-39}
Lead (II) iodide	PbI_2	8.5×10^{-9}
Lead (II) sulfide	PbS	3.0×10^{-28}
Magnesium carbonate	$MgCO_3$	6.8×10^{-6}
Magnesium hydroxide	$Mg(OH)_2$	5.6×10^{-12}
Silver (I) chloride	$AgCl$	1.8×10^{-10}
Silver (I) bromide	$AgBr$	5.4×10^{-13}
Silver (I) iodide	AgI	8.5×10^{-17}
Silver (I) chromate	Ag_2CrO_4	1.1×10^{-12}
Silver (I) sulfate	Ag_2SO_4	1.2×10^{-5}
Zinc (II) sulfide	ZnS	2.0×10^{-25}

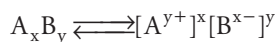
The experimental value of K_{sp} for $BaSO_4$ at 298 K is 1.1×10^{-10} . If the solubility of Ba^{2+} and SO_4^{2-} ions is 's' g mol/ liter (\because 1 g mol of $BaSO_4$ gives one g mol of Ba^{2+} ions and one g mol of SO_4^{2-} ions) then

$$1.1 \times 10^{-10} = s \times s = s^2$$

$$s = \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}$$

Hence the molar solubility of barium sulphate will be equal to 1.05×10^{-5} mol/liter.

In general, for the electrolyte A_xB_y which ionises as



The solubility product is given by

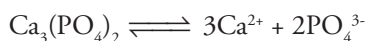
$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

where $[A^{y+}]^x$ and $[B^{x-}]^y$ are the ionic concentration in mole per liter in a saturated solution at a given temperature.

If the molar solubilities of A and B is 's' mol/liter, then

$$\begin{aligned} K_{sp} &= [xs]^x [ys]^y \\ &= x^x \cdot y^y (s)^{x+y} \\ (s)^{x+y} &= \frac{K_{sp}}{x^x \cdot y^y} \quad \text{or} \quad s = \left(\frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}} \end{aligned}$$

Consider the salt $\text{Ca}_3(\text{PO}_4)_2$ which dissociates to give three Ca^{2+} ions and two PO_4^{3-} anions. If the molar solubility of calcium phosphate is 's', then



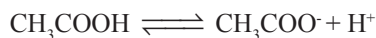
$$K_{sp} = (3s)^3 (2s)^2$$

$$K_{sp} = 108 s^5$$

$$\text{or } s = (K_{sp}/108)^{1/5}$$

9.8 Common Ion Effect

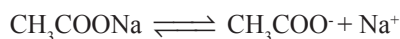
Let us consider the dissociation of a weak electrolyte say CH_3COOH . It dissociates to a very small extent



The equilibrium constant is given by

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

If a strong electrolyte say CH_3COONa having an ion common with this weak electrolyte is added to the solution then the concentration of CH_3COO^- ions will increase in the solution



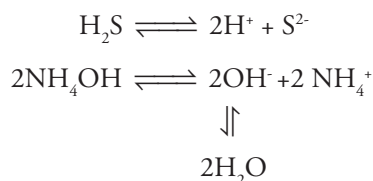
This results in an increase in the value of numerator which will increase the value of K. Since the value of K is constant at a given temperature, the reaction will proceed in the backward direction suppressing the dissociation of CH_3COOH .

This suppression of dissociation of a weak electrolyte by a strong electrolyte having an ion common with the weak electrolyte is termed as *common ion effect*.

Application of common ion effect and solubility product in qualitative inorganic analysis:

1. **Precipitation of sulphides:** The reagent for group II is H_2S in presence of dil HCl . Due to the presence of common H^+ ions, HCl suppresses the ionisation of H_2S . Under these conditions only metal sulphides of group II, which have low solubility product values (less than 1×10^{-28}) get precipitated.

Metal sulphides of group IV have high solubility product (greater than 1×10^{-25}) and therefore they require large sulphide ion concentration which is attained by passing H_2S in presence of NH_4OH .



The removal of H^+ ions as H_2O favours ionisation of H_2S producing greater concentration of sulphide ion.

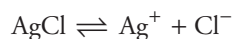
2. **Precipitation of hydroxides in group III:** The reagent for group III is NH_4OH in presence of NH_4Cl . The common NH_4^+ ion suppresses the ionisation of NH_4OH , hence the concentration of OH^- ions remains low, such that only hydroxides of iron, aluminium and chromium are precipitated. Since the solubility product of $\text{Mn}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ is high they are not precipitated in group III.

Solved Examples

1. Calculate the solubility product constant K_{sp} for AgCl if the solubility of silver chloride in water at 298 K is $1.35 \times 10^{-5} \text{ mol dm}^{-3}$.

Solution

AgCl dissociates in water as follows:

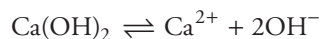


$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (1.35 \times 10^{-5})(1.35 \times 10^{-5}) = 1.82 \times 10^{-10}$$

2. If the K_{sp} value for $\text{Ca}(\text{OH})_2$ at 298 K is 4.7×10^{-6} , find its solubility in water.

Solution

The equilibrium reaction for $\text{Ca}(\text{OH})_2$ is



If s is the solubility of $\text{Ca}(\text{OH})_2$ in water then we see from the above equilibria that the concentration of OH^- is twice that of Ca^{2+} ions; hence

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

$$\text{or } K_{\text{sp}} = (s)(2s)^2 = 4s^3$$

$$s = \left(\frac{K_{\text{sp}}}{4} \right)^{\frac{1}{3}} = \left(\frac{4.7 \times 10^{-6}}{4} \right)^{\frac{1}{3}} = 1.1 \times 10^{-2} \text{ mol dm}^{-3}$$

Practice problems

1. If the solubility of $\text{Fe}(\text{OH})_2$ in water at 298 K is $2.3 \times 10^{-6} \text{ mol dm}^{-3}$, find the value of K_{sp} .
[Ans 4.9×10^{-17}]
2. If the K_{sp} value of $\text{Fe}(\text{OH})_3$ at 298 K is 2.6×10^{-39} , calculate its solubility.
[Ans 99×10^{-12}]

9.9 Oxidation and Reduction

Oxidation and reduction is an important concept in chemistry. We come across various oxidation reduction reactions in our daily life, like rusting of iron, generation of electricity in batteries, extraction and purification of metals and so on.

Classical concept defines oxidation as the addition of oxygen (or any other electronegative atom) or removal of hydrogen (or any electropositive atom). Oxidation has also been defined as the loss of electrons and reduction is defined as the gain of electrons. A substance that loses electrons is said to be oxidized and it acts as a reducing agent. On the other hand, a substance that gains electrons is said to be reduced and it in turn acts as an oxidizing agent.

9.10 Oxidation Number (Oxidation State)

Oxidation number or oxidation state expresses the combining capacity of an element. It is defined as the charge that an atom appears to have when electrons on the atom are counted according to the following conventions.

1. Electrons shared between two similar atoms are divided equally between them.
2. Electrons shared between two dissimilar atoms are counted with the more electronegative atom.
3. In electrovalent compounds the oxidation number is equal to the charge on the ion. The sum of oxidation number of all the atoms in the formula of an electrovalent compound is zero.

Some operational rules to calculate oxidation number have been derived on the basis of above convention.

1. Oxidation number of an element in uncombined state is zero.
2. Oxidation number of an ion is the same as the charge on it.
3. The sum of oxidation number of all the atoms in a neutral compound is zero.
4. The oxidation number of hydrogen per atom in all compounds is +1, except hydrides of active metals where the oxidation number of hydrogen is -1.

5. Oxidation number of oxygen per atom is -2 except in peroxides where it is -1 and superoxides where it is -1/2.

A given species is said to be oxidized if its oxidation number increases and is said to be reduced if its oxidation number decreases.

The application of oxidation and reduction for generation of electricity in galvanic cells, electrode potential, Nernst equation have been dealt with in detail in Chapter 16 on Electrochemistry and the role of oxidation and reduction reaction in corrosion has been discussed in detail in Chapter 3 on corrosion. In this chapter, we will discuss the application of principles of oxidation and reduction in metallurgy.

9.11 Application of Principles of Oxidation and Reduction in Metallurgy

Metals generally occur in nature in compound form as oxides, sulphides, carbonates, etc. Very few metals like silver, gold and platinum occur free, that is, in native state.

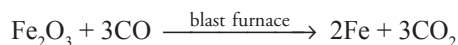
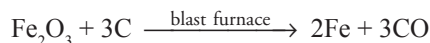
Noble metals are found in native state because their standard electrode potential (i.e., reduction potential) are always positive which implies that they have a tendency to accept electrons and reduce to corresponding metals. On the other hand, the standard electrode potential of active metals is negative hence they have a tendency to get oxidized (lose electrons) and combine with other elements in nature to form compounds. These compounds are called minerals. Minerals from which metal can be conveniently and economically extracted are called ores.

Although the conversion of ores to metals involves many steps but we shall discuss the extraction of metals only in terms of oxidation and reduction which involves the change in oxidation number of metals from an integer (in their ores) to zero (in their elemental state).

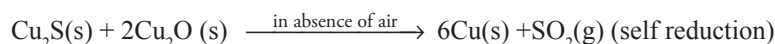
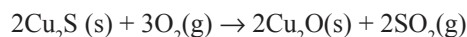
Reduction of oxide to the metal

1. **Chemical reduction:** The metal oxides are reduced to metals by heating them with a suitable reducing agent (C or CO or even another metal).

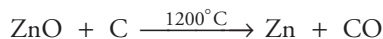
The roasted ore is mixed with carbon (coal or coke) and heated to a temperature above the melting point of the metal. Carbon and also carbon monoxide (produced by the incomplete combustion of coal) reduce the oxide to the free metal. For example



Sulphide ores of metals like Pb, Cu and Sb are first roasted to convert them partially into oxides, after sometime, air supply is cut off; self reduction of oxide and sulphide occurs giving the metal. For example

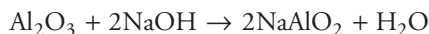


Similarly Zn is obtained by heating ZnO with coke

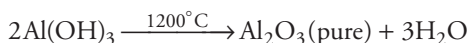
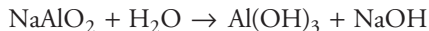


2. **Electrolytic reduction:** The carbon reduction method is not applicable for chemically active metals like alkali metals, alkaline earth metal, aluminium, etc. These metals are generally extracted by the electrolysis of their oxides. The pure metal is liberated at the cathode. Metals like copper and zinc are obtained by the electrolytic reduction of aqueous solutions of their sulphates. Similarly, aluminium is obtained by the electrolysis of a fused mixture of Al_2O_3 and cryolite $\text{Na}_3[\text{AlF}_6]$.
3. **Electrochemical extraction:** Highly electropositive metals like aluminium are extracted electrochemically. Ellingham diagram (discussed in Section 9.12) shows that reduction of Al_2O_3 with C is feasible only above 2400°C which is uneconomical, therefore it is extracted economically by electrochemical method known as the Hall – Heroult process. For this process pure alumina (Al_2O_3) is produced from bauxite either by Baeyer's process or by Halls process.

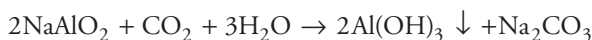
The following reactions are involved in Baeyers process:



(impurities of iron oxide, titanium oxide and silicates remain insoluble and are filtered off)



Reactions involved in Hall's process

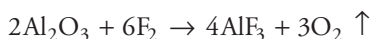


Electrolysis of alumina: Since the melting point of alumina is very high (2050°C) it is mixed with cryolite Na_3AlF_6 , which reduces the melting point to 1000°C . This melt is reduced electrolytically in a steel tank acting as cathode and having graphite rods as anode. The electrode reactions are complicated and not clearly understood but the probable reactions are as follows:

Aluminium fluoride from cryolite ionises as

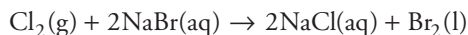


Aluminium is discharged at cathode, while fluorine reacts with Al_2O_3 at anode forming AlF_3 and liberating O_2 .

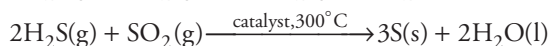
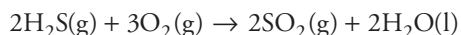


4. **Chemical oxidation:** Elements like sulphur, bromine and even gold are extracted by chemical oxidation. Let us discuss some examples.

The bromide ions in sea water are recovered by passing Cl_2 into sea water. Cl_2 displaces bromine from its solution as it comes above Br_2 in the electrochemical series.



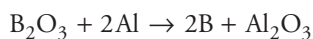
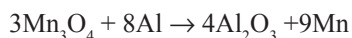
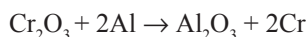
Similarly elemental sulphur is obtained from hydrogen sulphide by oxidation (Claus process). This process consists of two stages, the chemical equations of which are given below.



In the first stage, hydrogen sulphide is oxidised to sulphur dioxide which in the second stage reacts at $300^\circ C$ with more hydrogen sulphide in the presence of Fe_2O_3 or Al_2O_3 to give elemental sulphur.

5. **Other methods to reduce oxides to metals**

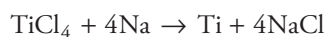
If the temperature required for the reduction of oxide by carbon is not easily attainable then the metal oxides are reduced by other metals such as aluminium. This is called the Goldschmidt thermite process. Common example are



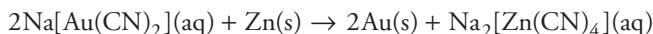
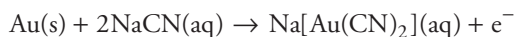
Displacement of one element by another

As studied in the chapter on electrochemistry, an element which is higher in the electrochemical series can displace another from its solution. This principle is used to extract elements. Let us discuss a few examples.

1. Mg and Na are used to reduce chlorides which are very stable.

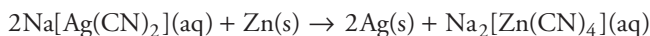


2. Although gold occurs in nature in native state, the metal is extracted from low grade ores by displacement with zinc. Gold is dissolved by reaction with NaCN and then displaced with zinc which is more reactive than gold and appears above it in the electrochemical series. The reactions involved are as follows:

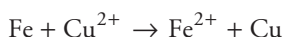


Alternative methods are used for the extraction of gold due to the toxicity of cyanide.

3. Silver can also be extracted by displacement with Zn:



- 4) Roasting cannot be used to extract copper from ores containing very small quantity of CuS. Such ores are left for weathering so that copper forms a solution of CuSO_4 in the presence of air and rain. Now iron is used to displace copper metal from its solution as iron is above copper in the electrochemical series.



In some cases like in case of Ag_2O_3 , reduction is carried out by the thermal decomposition alone.

9.12 Ellingham Diagram: Thermodynamical Aspect of the Reduction Process

H.J.T. Ellingham first used the free energy consideration (Gibbs energy) to explain the reduction of metal oxide to metal graphically. The graphic representation termed as the Ellingham diagram provides a sound basis for considering the choice of reducing agent for the reduction of metal oxides.

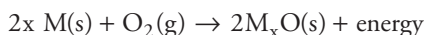
According to the law of thermodynamics the change in Gibbs energy ΔG for any process at a specified temperature is given by the equation

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the change in enthalpy, ΔS is the change in entropy and T is the absolute temperature.

A chemical reaction will be feasible and will occur spontaneously if free energy change ΔG is negative.

Consider a general reaction for the formation of metal oxide.



The above reaction is exothermic hence the value of ΔH is negative. In the above reaction a solid reactant and a gaseous reactant combine to give a solid product, hence the entropy of the

reaction decreases from left to right or in other words ΔS is negative. For such a condition where ΔS is negative the second term, $T\Delta S$ becomes positive and since $T\Delta S$ is to be subtracted from ΔH hence as the temperature increases ΔG become less and less negative. Thus the free energy change increases with rise in temperature. Figure 9.1 shows the free energy change ΔG with temperature for metal-metal-oxide reactions (based on 1 g mol of oxygen in each case).

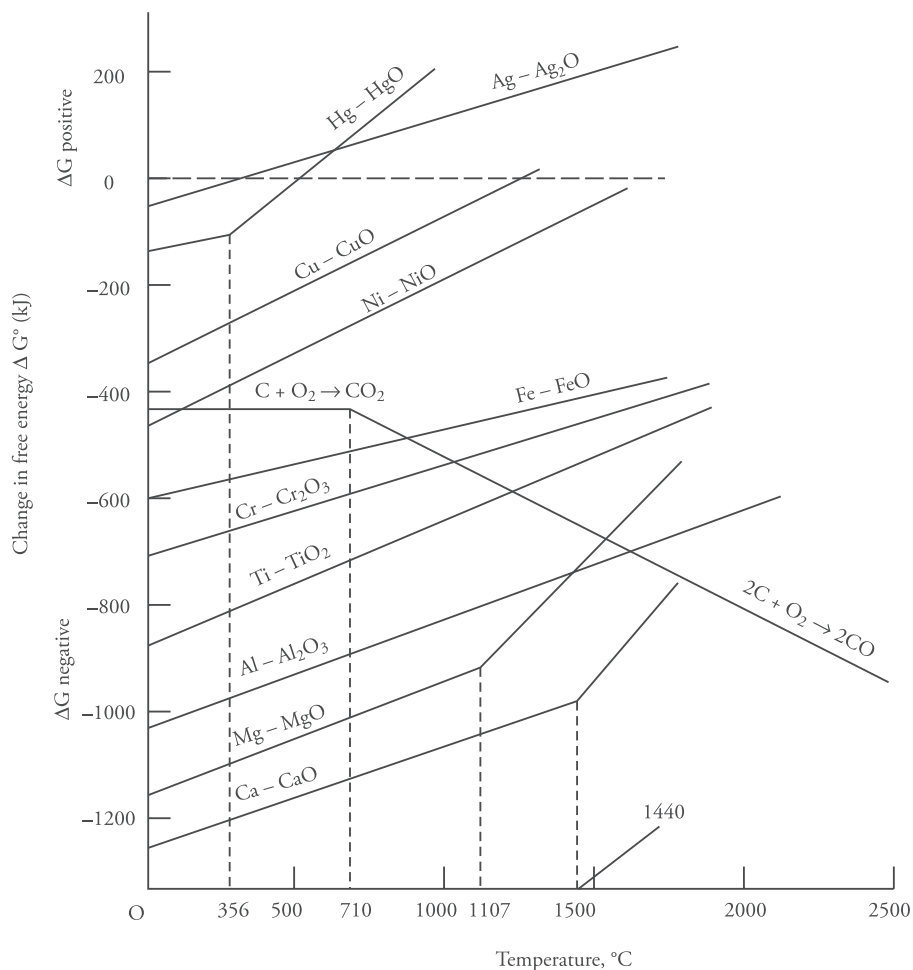


Figure 9.1 Ellingham diagram showing the change in free energy ΔG with temperature for metal-metal oxides reactions, based on one mole of oxygen in each case

This figure is known as Ellingham diagram and such diagrams can also be constructed for the conversion of metal to metal sulphide or metal halide using one mole of sulphur or halogen as the case may be.

On differentiating the equation $\Delta G = \Delta H - T\Delta S$ with respect to T (assuming that ΔH does not vary with change in temperature), we get

$$\frac{d(\Delta G)}{dT} = -T\Delta S$$

If ΔS for a reaction is negative the slope of the line obtained by plotting ΔG vs T will be positive and if ΔS for the reaction is positive then the slope of the line will be negative.

As discussed earlier for the formation of metal oxide (solid) from metal(solid) and oxygen(gas) ΔS is negative; hence the slope of line obtained by plotting ΔG vs T will be positive.

The Ellingham diagram for oxidation of metal to metal oxides has some key features:

1. All ΔG vs T lines slope upwards; hence as temperature rises the value of ΔG increases and becomes less and less negative.
2. The above trend is observed only as long as the metal is in solid state. If there is change in phase (metal undergoes fusion or vaporisation), the molecular entropy increases and the slope of ΔG vs T lines changes considerably. Thus the slopes of $\text{Hg} - \text{HgO}$, $\text{Mg} - \text{MgO}$ and $\text{Ca} - \text{CaO}$ lines change considerably at 356°C , 1107°C , 1440°C which are the boiling points of Hg , Mg and Ca , respectively.
3. As the temperature increases continuously, a state may arise where the ΔG vs T graph crosses the $\Delta G = 0$ line. Below this line ΔG is negative; hence metal oxide is stable but above this line ΔG is positive; hence the metal oxide becomes unstable and decomposes to give metal and oxygen. According to Ellingham diagram, theoretically all metal oxides should decompose to metal and oxygen at temperature where ΔG becomes positive; however, practically this does not happen because such temperatures are not easily attainable.

The oxides of Ag , Au and Hg are the only oxides that can decompose at temperatures that are easily attainable hence these metals can be extracted by thermal decomposition of their oxides (pyrometallurgy).

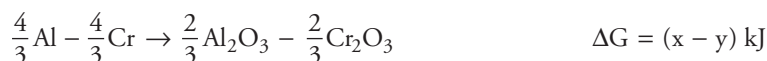
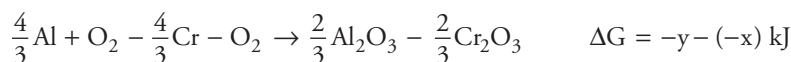
4. Very often one metal is used to reduce the oxide of another metal. Aluminium reduces Cr_2O_3 to Cr . A metal reduces the oxide of other metal which lies above it in the Ellingham diagram. This can be illustrated as follows.

Consider the following reaction taking place at a particular temperature.



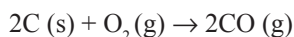
Considering the ΔG vs T slopes in the Ellingham diagram we see that the slope of $\text{Al} - \text{Al}_2\text{O}_3$ lies below the slope of $\text{Cr} - \text{Cr}_2\text{O}_3$ system.

Subtracting Eq. (1) from (2) we get



Since $y > x$, hence $(x-y)$ is negative and ΔG accompanying reaction (3) is negative making the reaction thermodynamically feasible, hence Al will reduce Cr_2O_3 to Cr. The reverse reaction, that is, reduction of Al_2O_3 by Cr will not occur because ΔG in that case would be positive and hence the reaction will not be feasible. However, Mg – MgO line lies below Al – Al_2O_3 line in Ellingham diagram, hence Mg will reduce Al_2O_3 to Al.

- From the Ellingham diagram let us consider the ΔG vs T slopes for the reaction of carbon with oxygen. There are two possibilities.



In the first reaction ΔS is zero (volume of CO_2 produced is equal to the volume of O_2 used) hence ΔG vs T line is parallel to the temperature axis. In the second reaction ΔS is positive (two volumes of CO are produced for one volume of O_2 used) hence the ΔG vs T slope is negative. The two curves cross each other at about 710°C (Fig 9. 1). Metal oxides which lie above the horizontal line in Ellingham diagram are reduced to metal at a temperature below 710°C and carbon gets oxidised to CO_2 . Above 710°C carbon is oxidised to CO. Moreover above 710°C ΔG vs T line for $\text{C} \rightarrow \text{CO}$ slopes downwards and eventually crosses all metal–metal oxide graphs which lie below this line. This means that in principle carbon can be used to reduce any metal oxide to metal provided sufficiently high temperature is made available. This is sometimes difficult to achieve and hence other techniques are used for the reduction of metal oxides to metals.

Iron is obtained from its oxide ore by heating it with carbon at temperature around 1000°C at which the C- CO line lies below the Fe –FeO line (Fig. 9.1).

The reduction of SiO_2 with C is extremely difficult as the temperature at which C can reduce SiO_2 is very high, that is, around 1500°C (Si – SiO_2 line is not shown in the diagram).

If extremely high temperatures are required for reduction of metal oxides, then they are reduced electrolytically. In this method the process of reduction of metal oxides is coupled with another process for which ΔG is sufficiently negative, so that the overall ΔG for the coupled reaction becomes negative and the reaction becomes feasible.

Limitations:

There are two main limitations of the Ellingham diagrams:

- It predicts feasibility of the reaction and says nothing about the speed of the reaction.
- It is based on the assumption that the reactants and products are in equilibrium which is not true.

9.13 Molecular Interactions

Interactions between the atoms leads to the formation of molecules. These molecules may be formed by the complete transfer of electrons (electrovalent or ionic bond) having strong electrostatic attraction between the atoms or they may be formed by the sharing of electrons (covalent bond).

Attractive and repulsive forces not only exist between the bonded atoms but they also exist between the non bonded atoms. The different types of forces that exist between the molecules are the intermolecular forces and those within the molecule are the intramolecular forces. These forces are responsible for various properties like bond lengths, melting and boiling points, surface tension and viscosity. They are also responsible for the formation of condensed phases and large molecular assemblies. Let us discuss these molecular interactions one by one.

Intermolecular forces

These are the forces of attraction and repulsion between polar and non polar molecules. They generally operate between the non-bonded molecules and are termed as the van der Waals forces. These interactions can be of different types which are as follows.

1. *Ion–dipole interactions:* These interactions are observed between an ion (point charge) and a point dipole. A point dipole is one in which the charge separation in the polar molecule is much less than the distance between the point charge and the distance at which the dipole is observed ($l \ll r$) (Fig. 9.2). These interactions are similar to ion–ion interactions (ionic bonds), except that they are somewhat weaker than them and are more affected by distance ($1/r^2$ instead of $1/r$). The potential energy of interaction between an ion and a dipole is

$$U = -\frac{Z^{\pm}\mu}{4\pi\epsilon_0 r^2}$$

where Z^{\pm} is the charge on the ion, r is the distance between the ion and point dipole, μ is the dipole moment of the polar molecule. These forces are observed in solutions of ionic compounds in polar solvents where solvated species such as $\text{Na}(\text{OH}_2)_x^{+}$ and $\text{F}(\text{H}_2\text{O})_y^{-}$ exist when NaF is dissolved in water.

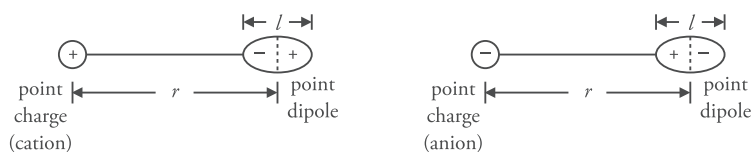


Figure 9.2 *Ion dipole interaction*

2. *Dipole–dipole interactions:* In polar molecules having permanent dipoles (such as H_2O , HF , HCl), the van der Waals forces are mainly due to electrical interaction between the dipoles known as dipole–dipole interaction. In these molecules the centres of positive and negative charges are different and they align themselves in such a way that the opposite charge of the two molecules come closer to each other. The potential energy for the dipoles arranged as shown in Figure 9.3 is given by

$$U = -\frac{\mu_1\mu_2}{2\pi\epsilon_0 r^3}$$

where μ_1 and μ_2 are the dipole moments of the two different molecules and as discussed in the previous case, $l \ll r$. For parallel orientation the potential energy of interaction between the two molecules is given by the formula.

$$U = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\epsilon_0 r^3} \quad f(\theta) = 1 - 3\cos^2 \theta$$

Dipole–dipole interactions are weaker than ion–dipole interactions and fall off more rapidly with distance ($1/r^3$). Like ion–dipole interactions these forces are also directional and are responsible for associations in polar liquids like water and hydrogen fluoride. Gases like ammonia and sulphur dioxide can be easily liquefied due to these interactions.

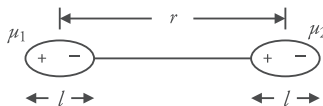


Figure 9.3 (a) Dipole–dipole interactions

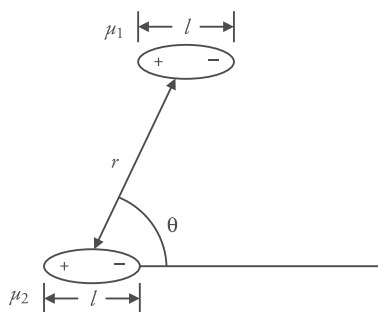


Figure 9.3 (b) Dipole–dipole interactions with parallel orientation of dipoles

3. Induced dipole interactions: These are of two types

- (a) *Ion–induced dipole*: An ion in the neighbourhood of a neutral molecule will distort its electron cloud and will induce a dipole in the neighbouring molecule. The distortion (termed as polarisation) of the molecule will depend upon the polarisability α and on the polarising field of the charge ion. The energy of interaction is given by

$$U = -\frac{1}{2} \frac{Z^2 \alpha}{r^4} \quad \text{or} \quad U \propto \frac{1}{r^4}$$



Figure 9.4 Ion-induced dipole interactions

- (b) *Dipole–induced dipole*: A polar molecule (dipole) can also induce a dipole in a non-polar molecule. The induced dipole of the latter interacts with the permanent dipole of the

former and the two are attracted towards each other. The interaction energy is given by

$$U = -\frac{\mu^2 \alpha}{r^6} \quad \text{or} \quad U = \frac{1}{r^6}$$

Since the energy is inversely proportional to r^6 hence they are effective only at very short distances. These forces are responsible for the solubility of polar compounds in non polar solvents.

4. *Induced dipole–induced dipole interactions:* The existence of non –polar diatomic molecules like O_2 , N_2 and non polar monoatomic molecules like such as He, Ne, Ar, etc. into solid and liquid state could not be explained by the molecular interactions discussed above. F. London in 1930 provided a satisfactory explanation for the existence of attractive forces between these non – polar molecules. According to London, the electrons in a non-polar molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this the electrons may flicker to a position such that the positive charge may be concentrated in one region and the negative charge in other region. This arrangement gives the molecule an instantaneous dipole. This dipole in turn polarises the neighbouring molecule and induces an instantaneous dipole in it. Since the electrons around the nucleus of the first atom are continuously oscillating so the direction of the instantaneous dipole changes which leads to a simultaneous change in the induced dipole of the neighbouring molecule. These interactions between instantaneous dipole of one molecule and induced dipole of the other molecule is termed as the London forces or dispersion forces. The strength of dispersion forces depends upon the polarisability of the molecules. The energy is given by the London formula

$$U = -\frac{3\alpha_1\alpha_2 I_1 I_2}{2r^6 (I_1 + I_2)}$$

where I_1 and I_2 are the ionisation potential of the two molecules. Thus the interaction energy is inversely proportional to the sixth power of the distance between adjacent molecules.

London dispersion forces could successfully explain the trends in boiling points of noble gases.

9.14 Real Gases and Critical Phenomenon

An ideal or perfect is one which obeys the different gas laws like Boyle's law ($PV = \text{constant}$ at constant temperature), Charles law ($V \propto T$ at constant P) and Avogadro's law (equal volume of all gases under same temperature and pressure contains equal number of molecules) under all the conditions of temperature and pressure. An ideal gas obeys the gas equation $PV = nRT$.

These gas laws were postulated assuming that the volume of the gas particles is negligible in comparison to total volume occupied by the gas and that there are no inter molecular forces of attraction and repulsion between the molecules and between the molecules and walls of the container.

These assumptions hold good only when the gas molecules are far from each other and this happens only at low pressure or high temperature. However if the pressure is high or temperature is low the gas molecules come close together and in such a case the intermolecular forces of attraction and repulsion cannot be considered as negligible. Also under high pressure and low temperature the volume of the gas is so small that the volume occupied by the gas molecules cannot be neglected. This leads to deviations from ideal behavior.

For an ideal gas $PV = \text{constant}$ (Boyle's law) hence at constant temperature the product of PV should be constant at all pressures and the plot of PV vs P should be a horizontal line parallel to the x -axis (Fig. 9.5).

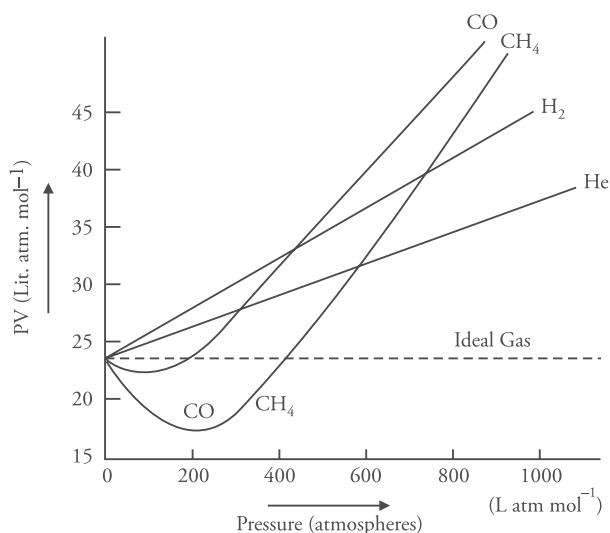


Figure 9.5 Plots of PV vs P for different gases at 0°C (273 K)

From the graph it is seen that two type of curves are obtained.

- For gases like CO and CH_4 , the product PV first decreases with increase of pressure, reaches a minimum and then increases.
- For gases like H_2 and He the product PV continuously increases with increase in pressure.

van der Waals applied the pressure and volume corrections for real gases and obtained the van der Waals equation of state for real gases.

- (i) **Volume correction:** van der Waals said that the volume occupied by a gas is not negligible compared to the total volume of the gas. He introduced a parameter b as a measure of minimum volume occupied by a mole of the gas, hence the total volume available to the gas molecules for movement is $V-nb$ instead of volume V . He replaced the perfect gas law $P = nRT/V$ by $P = nRT/(V-nb)$

n is the number of moles of the gas. This term nb is called the excluded volume and the volume b per mole is also known as covolume. Calculations show that the excluded volume per molecule is four times the actual volume of the gas molecules.

$$\text{or } b = 4 \times V_{\text{molecule}} \times N_A \quad (N_A = \text{Avogadro number})$$

- (ii) **Pressure correction:** If a molecule say X is lying in the middle of the vessel then it will be attracted equally on all sides of the neighboring molecules so that there is no resultant attractive force on the molecule. However, if a molecule like Y lies near the walls of the container it experiences a net attractive force of the molecules in the bulk of molecules behind it. This net attractive force reduces both the frequency and force of collisions with the walls of the container. The strength of attractive force is proportional to the molar concentration n/V of molecules in the sample and the reduction of pressure is proportional to $(n/V)^2$

$$P \propto (n/V)^2$$

$$P = a (n/V)^2$$

where a is a positive constant characteristic of a gas and is a measure of the strength of the attractive forces. The corrected pressure becomes $P + a (n/V)^2$.

Combining both the attractive and repulsive effects, the van der Waals equation of state can be written as

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Table 9.4 van der Waals constants for some common gases

Gas	$a \text{ (dm}^6 \text{ atm mol}^{-2}\text{)}$	$b \text{ (dm}^3 \text{ mol}^{-1}\text{)}$	Gas	$a \text{ (dm}^6 \text{ atm mol}^{-2}\text{)}$	$b \text{ (dm}^3 \text{ mol}^{-2}\text{)}$
Ammonia	4.17	0.0371	Hydrogen chloride	3.67	0.0408
Argon	1.35	0.0322	Neon	0.21	0.0171
Carbondioxide	3.59	0.0427	Nitrogen	1.39	0.0319
Chlorine	6.49	0.0562	Oxygen	1.36	0.0318
Helium	0.034	0.0237	Sulphur dioxide	6.71	0.0564
Hydrogen	0.246	0.0266	Nitrogen dioxide	5.28	0.0442

Discussion of van der Waals equation:

- (i) *At very low pressure:* At very low pressures the molecules of gas are far apart and intermolecular attractive forces can be regarded as negligible. Also the volume of gas is very large, hence both a/V^2 and nb can be neglected. That is why at extremely low pressures the gases follow the ideal gas equation.
- (ii) *At moderate pressure:* With increase in pressure, the volume decreases and hence the factor a/V^2 increases and can no longer be neglected. However, at moderate pressure, the volume V is still quite large in comparison to b which can be neglected. Hence, the van der Waals equation reduces to

$$(P + a/V^2)V = RT$$

$$\text{or, } PV = RT - a/V$$

Thus the product PV is less than RT by an amount equal to a/V . As pressure increases V decreases and a/V increases, therefore PV become smaller and smaller. This explains the dip in the plots isotherms of gases like carbon monoxide, methane and ammonia (see Fig 9.5).

- (iii) *At high pressure:* At very high pressure, the volume V is quite small and in such a condition it is not possible to ignore b . Since P is very high, the pressure correction factor a/V^2 becomes negligible in comparison to P and therefore the van der Waals equation reduces to

$$P(V - b) = RT$$

$$PV = RT + Pb$$

Thus PV is greater than RT by an amount equal to Pb . As pressure increases the product Pb increases, thereby increasing PV . This explains why the value of PV increases after reaching a minimum.

- (iv) *At high temperature:* At a given pressure when the temperature is considerably high the volume becomes larger making the value of a/V^2 sufficiently small. Moreover, when V is large b can be neglected in comparison to V . Hence at high temperature the van der Waals equation reduces to $PV = RT$.

Exceptional behavior of hydrogen and helium: The masses of both hydrogen and helium are very small; hence the intermolecular forces of attraction between these molecules are extremely small even at high pressure which is reflected in the small values of van der Waals constant a for these gases. As a result the correction term a/V^2 remains negligible at ordinary temperature and at all pressures. The van der Waals equation reduces to

$$P(V - b) = RT \text{ or } PV = RT + Pb$$

This is the reason why hydrogen and helium show positive deviations only and product PV increases continuously with the rise in pressure.

Thus we see that the van der Waals equation satisfactorily explains the behavior of real gases.

Critical Phenomenon:

At normal condition of pressure and temperature the gas molecules remain independent of each other. As the temperature is reduced or pressure is increased the gas molecules come close to each other and experience the force of attraction. Gradually on lowering the temperature or increasing the pressure, the molecules come closer and closer and finally the gas liquefies. Hence normally increase in pressure or decrease in temperature brings about liquefaction of gases. For example sulphur dioxide can be liquefied at -8°C at a pressure of 1 atm; if the pressure increases to 3.24 atm sulphur dioxide can be liquefied at a higher temperature of 20°C if the pressure increases to 3.24 atm sulphur dioxide can even be liquefied at a higher temperature of 20°C . The effect of temperature is more important than that of pressure because for each gas there is a temperature above which it cannot be liquefied no matter how high the pressure is applied. This temperature is termed as the critical temperature (T_c), which is different for different gases. For example the critical temperature of carbon dioxide is 31.1°C which means that it is impossible to liquefy carbon dioxide above 31.1°C by any means. At critical temperature a certain pressure is required to liquefy

the gas. This minimum pressure required to liquefy the gas at critical temperature is called the critical pressure (P_c) and the volume occupied by a gas at critical temperature and pressure is called the critical volume (V_c). For a particular gas, the critical temperature, critical pressure and critical volume are termed as its critical constant. The critical constant for carbon dioxide are $T_c = 31.1^\circ\text{C}$, $P_c = 72.9\text{ atm}$, $V_c = 94\text{ mL/mol}$.

Similarly the critical temperature of oxygen are $T_c = -118^\circ\text{C}$, $P_c = 50.1\text{ atm}$ and $V_c = 78.2\text{ mL/mol}$ and for hydrogen T_c is -240°C , $P_c = 12.8\text{ atm}$ and $V_c = 65.5\text{ mL/mol}$.

Solved Examples

- Calculate the pressure exerted by two moles of carbon dioxide gas in a 1.35 dm^3 vessel at 45°C using (i) ideal gas equation (ii) van der Waals equation

Given: van der Waals constant $a = 3.59\text{ dm}^6\text{ atm mol}^{-2}$; $b = 0.0427\text{ dm}^3\text{ mol}^{-1}$

Solution

- For an ideal gas $PV = nRT$

$$P = \frac{nRT}{V}$$

$$= \frac{(2\text{ mol})(0.0821\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1})(318\text{ K})}{1.35\text{ dm}^3} = 38.67\text{ atm}$$

- For van der Waals gas

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or } P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$= \frac{(2\text{ mol})(0.0821\text{ dm}^3\text{ atm K}^{-1}\text{ mol}^{-1})(318\text{ K})}{(1.35\text{ dm}^3) - (2\text{ mol})(0.0427\text{ dm}^3\text{ mol}^{-1})} - \frac{(3.59\text{ atm dm}^6\text{ mol}^{-2})(2\text{ mol})^2}{(1.35\text{ dm}^3)^2}$$

$$= 50.951\text{ atm} - 10.637\text{ atm}$$

$$= 40.314\text{ atm}$$

Practice problems

- Calculate the pressure exerted by three moles of ammonia gas enclosed in a vessel of capacity 6 liters at a temperature of 30°C assuming that

(a) The gas behaves as an ideal gas

(b) The gas behaves as a real gas

Given $a = 4.17\text{ atm liter}^2\text{ mol}^{-2}$ or $4.17\text{ atm dm}^6\text{ mol}^{-2}$; $b = 0.037\text{ liter mol}^{-1}$ or $b = 0.037\text{ dm}^3\text{ mol}^{-1}$

[Ans (a) 12.438 atm (b) 67.696 atm]

Summary

- Different investigators gave different definitions of acid and base. Arrhenius defined acid as a proton donor and base as a substance that dissolves in water to yield hydroxyl ions. Bronsted–Lowry defined acid as a proton donor and base as a proton acceptor. Lewis defined acid as an electron pair acceptor and base as an electron pair donor.
- Hard soft acids and bases concept was given by Pearson. Soft acids are electron acceptors that have high polarisability, have low positive charge, low electronegativity and do not have a noble gas configuration.
Hard acids: Small in size, high electronegativity, low polarisability with a noble gas configuration.
Soft bases: Have low electronegativity and are easily polarised.
Hard bases: Have high electronegativity and low polarisability.
Stable compounds are formed when both acid and base are either hard or soft.
- Common ion effect is the suppression of dissociation of a weak electrolyte by a strong electrolyte having an ion common with the weak electrolyte.
- Solubility product and common ion effect have application in qualitative inorganic analysis.
- Oxidation number or oxidation state express the combining capacity of an element.
- Oxidation and reduction finds use in the generation of electricity in galvanic cells, corrosion, electrochemistry and metallurgical operations.
- Ellingham diagram shows the change in free energy ΔG with temperature for metal – metal oxide reactions based on one mole of oxygen in each case. It helps in predicting the feasibility of thermal reduction of ore.
- Different type of intermolecular forces exist between polar and non polar molecules like the ion- dipole interaction, dipole-dipole interaction, ion-induced dipole interaction, dipole- induced dipole interaction, induced dipole- induced dipole interaction.
- The principle of oxidation and reduction used for the extraction of metals. Metals can be extracted by displacement of one element with another, chemical oxidation, electrochemical extraction.
- The ideal gas equation $PV=nRT$ is obeyed by gases at low pressure or high temperature. At high pressure and low temperatures the real gas equation (van der Waals equation $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ is followed.
- The temperature above which a gas will not liquefy no matter how high the pressure is called is critical temperature (T_c). The pressure of the gas at critical temperature is called its critical pressure (P_c) and the volume occupied by the 1 mole of a gas at critical temperature and pressure is termed as its critical volume (V_c).

Review Questions

1. Explain the Arrhenius concept of acid and base. What are its limitations?
2. “All Bronsted–Lowry acids and bases are also Lewis acids and Lewis bases, . But all Lewis acids and bases are not Bronsted – Lowry acid and base”. Justify the statement.
3. What do you understand by a conjugate acid – base pair. Write the conjugate acid / base of the following species.
 HNO_2 , CN^- , HClO_4 , F^- , OH^- , CO_3^{2-} , S^{2-} , NH_3 , CH_3COO^- , H_2CO_3 , H_2O
4. With the help of suitable examples explain that strong acids have weak conjugate base and weak acids have strong conjugate base.
5. Explain the Lewis concept of acids and bases, according to Lewis which type of species can act as acids and bases, illustrate with examples.
6. Explain the concept of hard and soft acids and bases. How is this concept helpful in predicting the occurrence of minerals in nature. On the basis of the concept explain why AgI_2^- is stable and AgF_2^- does not exist.
7. Define solubility product. Give an example for the solubility product of the salt A_xB_y .
8. What is meant by common ion effect. Discuss its application in quantitative inorganic analysis.
9. Calculate the oxidation number of the underlined element in each of the following.

(a) KMnO_4	(b) NH_4NO_3
(c) $\text{K}_3\text{Fe}(\text{CN})_6$	(d) OsO_4
(e) HNO_3	(f) KO_2
(g) KI_3	(h) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
(i) $\text{Fe}(\text{CO})_5$	(j) NOClO_4
10. Write a note on the different methods employed to obtain crude metal from their oxides.
11. What is an Ellingham diagram. How does it help in the selection of reducing agent to reduce the metal oxide into the metal.
12. What are ideal and real gases. Derive the van der Waals gas equation and discuss how the equation applies at different temperatures and pressures. Also explain what do you understand by critical phenomenon.

Multiple Choice Questions

1. The conjugate acid of a strong base is a

(a) Strong acid	(b) Weak acid
(c) Strong base	(d) Weak base
2. Cl^- ion is the conjugate base of

(a) HCl	(b) HOCl
(c) HClO_3	(d) HClO_4

3. Conjugate acid of OH^- base is
(a) H_2 (b) H_2O
(c) H^+ (d) H_3O^+
4. The conjugate acid of NH_2^- is
(a) NH_4^+ (b) NH_3
(c) NH_2OH (d) N_2H_4
5. Which of the following anions is the strongest base
(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^-
6. In the acid base reaction
 $\text{HCl} + \text{CH}_3\text{COOH} \rightleftharpoons \text{Cl}^- + \text{CH}_3\text{COOH}_2^+$ the conjugate acid of acetic acid is
(a) Cl^- (b) HCl
(c) $\text{CH}_3\text{COOH}_2^+$ (d) H_3O^+
7. The solubility of $\text{Al}(\text{OH})_3$ is 's' g mol/liter. Its solubility product is
(a) s^2 (b) $27s^3$
(c) s^3 (d) $27s^4$
8. Which among the following is a Lewis acid
(a) BF_3 (b) NH_2^-
(c) NH_3 (d) NH_4^+
9. Ammonia is a Lewis base because it is
(a) Electron pair donor (b) Electron pair acceptor
(c) Proton donor (d) Proton acceptor
10. In the conversion of Br_2 to BrO_3^- the oxidation state of bromine changes from
(a) 0 to +5 (b) 1 to 5
(c) 0 to -3 (d) 2 to 5
11. The oxidation state of Fe in iron pentacarbonyl is
(a) 1 (b) 2
(c) 0 (d) 2.5
12. Which of the following ore contains both Ca and Mg
(a) Lime stone (b) Dolomite
(c) Chalk (d) Feldspar
13. Which of the following methods is used for the concentration of sulphide ore
(a) Gravity separation (b) Froth flotation
(c) Magnetic separation (d) Leaching
14. Which of the following is reducing agent in thermite process
(a) Au (b) Na
(c) Al (d) Mg

15. The oil used as a frothing agent in froth flotation process is
 - (a) Pine oil
 - (b) Mustard oil
 - (c) Coconut oil
 - (d) Olive oil
16. Which of the following reaction is not a calcination reaction
 - (a) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
 - (b) $\text{ZnCO}_3(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{CO}_2(\text{g})$
 - (c) $2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g})$
 - (d) $\text{CaCO}_3 \cdot \text{MgCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{MgO}(\text{s}) + 2\text{CO}_2(\text{g})$
17. Ellingham diagram helps in –
 - (a) Predicting the feasibility of thermal reduction of the ore
 - (b) Selection of furnace for heat treatment of ore
 - (c) Selecting method for refining the ore
 - (d) Selecting method for concentration of the ore
18. Which of the following metal is refined by liquation
 - (a) Iron
 - (b) Copper
 - (c) Silver
 - (d) Lead
19. Which of the following is refined by zone refining
 - (a) Mg
 - (b) Ge and Si
 - (c) Ca
 - (d) Ni
20. Which of the following metal is thrown as anode mud during electrolytic refining of copper
 - (a) Zn
 - (b) Fe
 - (c) Ni
 - (d) Ag
21. Pearson defined hard base as one in which the donor atom has
 - (a) Low electronegativity, low polarisability and difficult to oxidise
 - (b) High electronegativity, high polarisability and easy to oxidise
 - (c) High electronegativity, low polarisability and is difficult to oxidise
 - (d) Low electronegativity, high polarisability and difficult to oxidise
22. According to Pearsons HSAB concept which of the following is a soft acid
 - (a) Ag^+
 - (b) I^+
 - (c) Sr^{2+}
 - (d) Al^{3+}
23. Which of the following is a hard acid according to Pearsons HSAB concept
 - (a) F^-
 - (b) I^-
 - (c) NO_3^-
 - (d) O_2^-
24. A real gas approaches ideal behavior at
 - (a) High temperature and low pressure
 - (b) Low temperature and low pressure
 - (c) Low temperature and high pressure
 - (d) High temperature and high pressure

25. Which of the following equation correctly represents the van der Waals equation

(a) $PV = RT$

(b) $\left(P + \frac{a}{V^2}\right)(V + b) = RT$

(c) $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

(d) $\left(P - \frac{a}{V^2}\right)(V + b) = R$

Solution

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (a) | 3 (b) | 4 (b) | 5 (a) | 6 (c) | 7 (d) | 8 (a) |
| 9 (a) | 10 (a) | 11 (c) | 12 (b) | 13 (b) | 14 (c) | 15 (a) | 16 (c) |
| 17 (a) | 18 (d) | 19 (b) | 20 (d) | 21 (c) | 22 (a) | 23 (b) | 24 (a) |
| 25 (c) | | | | | | | |

Chapter 10

ATOMIC STRUCTURE AND CHEMICAL BONDING

10.1 Introduction

The word atom owes its origin to the Greek word (atomos ‘indivisible’). It was believed that atom is the smallest particle that cannot be divided further. Later it was proved that atom is divisible, and hence the name may be inappropriate; however, it was retained. Atomic particles are made up of three basic subatomic particles: electron, proton and neutron. These particles are regarded as the fundamental particles. Many scientists attempted to explain the arrangement of these particles inside the atom. Thomson in 1898 suggested that the atom is a positively charged solid sphere and the electrons are embedded in it. This was the *plum pudding model* because it resembled a pudding with plums embedded in it. Later, Rutherford proposed another model known as the Rutherford’s model of an atom. According to this model, an atom consists of a positively charged center called the nucleus. The nucleus contains almost all the mass of the atom. The electrons, which are negatively charged, move around the nucleus in fixed paths. The space between the nucleus and electrons is empty. In 1913, Bohr gave the concept of stationary energy levels called orbits. He postulated that

- The electrons revolve around the nucleus in specific orbits. As long as the electron remains in a particular orbit it does not lose or gain energy.
- However, when an electron jumps from one orbit to the other it can either absorb energy or lose energy. Energy (as photon) is emitted if the electron jumps from an orbit of higher energy to an orbit of lower energy. This energy is given by $E_2 - E_1$, and the wavelength of the emitted radiation is given by the Einstein–Planck equation.

$$E_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

Similarly, on absorbing energy from some sources the electron can jump from lower energy to higher energy orbit.

The angular momentum l of the electron moving in a particular orbit is quantised and has definite values, which are whole number multiples of $\frac{h}{2\pi}$

$$l = \frac{nh}{2\pi}$$

This is termed as the Bohr's rule of quantisation.

Although Bohr's theory was successful, it had to be abandoned because of many shortcomings. de Broglie and Heisenberg later introduced the wave nature of electron in addition to its particle nature and pointed out that the path of motion of the electron cannot be well defined. These ideas gave a blow to the Bohr's concept of well-defined circular orbitals and led to the development of a new approach called wave mechanics.

10.2 Dual Nature of Radiation

The earliest view of light, as discovered by Newton, regarded light as being composed of small particles (commonly termed as corpuscles of light). This nature of light could explain the phenomenon of photoelectric effect but could not explain reflection, refraction, dispersion and interference. Later, Huygen proposed the wave-like character of light. The wave nature of light could explain the phenomenon of reflection, refraction, dispersion and interference. However, photoelectric effect and black body radiation could not be explained by the wave nature of light. In 1856, James Maxwell proposed that light and other forms of radiations propagate through space in the form of waves. These waves have electric and magnetic fields associated with them. Therefore, these radiations are known as electromagnetic radiations. Einstein, in 1905, suggested that light can behave both as a particle as well as a wave, that is, it has a dual nature. The particle nature of light successfully explains some properties of light, whereas the other properties and experimental findings can be successfully explained with the help of the wave nature of light.

10.3 Dual Nature of Matter: de Broglie Equation

When electrons were discovered, various experimental studies proved that they behave like a particle. Bohr had also treated electron as a particle. However, in 1924, Louis de Broglie (who received the Nobel prize for physics in 1929) suggested that just as light exhibits wave and particle properties, all microscopic particles in motion such as electrons, protons, atoms, ions, and molecule, etc., also have a dual character. Thus, according to de Broglie, all material particles in motion possess wave characteristics.

de Broglie deduced that the particle and wave properties are related by the expression

$$\lambda = \frac{h}{mv}$$

where h = Planck's constant; λ , m and v are, respectively, the wavelength, mass and velocity of the particle.

Derivation of de Broglie Relationship

If a particle of mass m is moving with a velocity v and the wavelength λ is associated with it, then de Broglie deduced a relation between these three parameters. He made use of Planck's quantum theory and Einstein theory. According to Planck, the energy E associated with the photon of frequency ν is given by the equation.

$$E = h\nu \quad (i)$$

According to Einstein, mass and energy are related as

$$E = mc^2 \quad (ii)$$

where c is the velocity of light.

Comparing (i) and (ii), we get

$$h\nu = mc^2$$

Since $\nu = \frac{c}{\lambda}$

$$\frac{hc}{\lambda} = mc^2$$

or $\frac{h}{\lambda} = mc$ or $\lambda = \frac{h}{mc}$

The equation $\lambda = \frac{h}{mc}$ is known as the de Broglie's equation. Replacing c by v for an electron or any other particle, we have $\lambda = h/mv$

$$\lambda = \frac{h}{p} = \frac{\text{Planck's constant}}{\text{momentum}}$$

where p stands for the linear momentum (mass \times velocity) of the particle and h is a constant.

$$\therefore \lambda \propto \frac{1}{\text{momentum}}$$

Thus, wavelength of a moving particle is inversely proportional to its momentum.

Experimental Verification of Dual Nature of Electrons

Dual nature of electrons was confirmed by the following experimental lines of evidence

1. **Particle nature of electrons** When a beam of electrons strikes a fluorescent zinc sulphide screen, it produces a spot of light known as scintillation. It has been observed that each striking electron produces only one scintillation point. This proves that the scintillation and, therefore, the striking electrons must be localised and not spread out like a wave. This suggests that the electron behaves as a particle.

2. **Wave nature of electrons** Wave nature of electrons was experimentally verified by C.P. Davisson and L.H. Germer in 1927. They found that when a beam of electrons was made to strike a nickel crystal, concentric dark and bright rings were formed. These rings were called diffraction rings and their patterns were similar to those observed by the diffraction of X-rays (de Broglie). As the pattern obtained by the diffraction of electrons is similar to that of X-rays, the electrons have wave character similar to the X-rays. Furthermore, the wavelengths of electrons calculated by diffraction experiments and those calculated by de Broglie's equation were found to be in agreement with each other. Similar diffraction patterns were obtained for protons, neutrons, hydrogen atoms, etc. This proves that all material particles have a wave-like character and hence a dual nature.

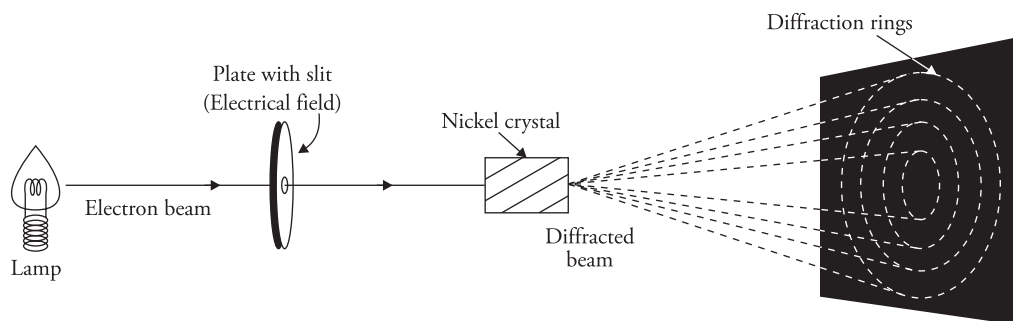


Figure 10.1 Electron diffraction experiment by Davisson and Germer

Derivation of Bohr's Postulate of Quantisation of Angular Momentum from de Broglie Relationship

Bohr postulated that when an electron moves in a particular orbit, its angular momentum is quantised. This can be explained with the help of de Broglie's equation. For this, let us consider an electron moving around the nucleus in the form of wave in a circular orbit of radius r . The electron wave may be **in phase** or **out of phase**. If the two ends of the waves meet to give a regular series of crests and troughs, they are said to be in phase (Fig. 10.2a) and if the two ends do not meet to give a regular series of crests and troughs they are said to be out of phase (Fig. 10.2b). As is clear from Figure 10.2 a, when the circumference of the circular orbit is an integral multiple of the wavelength, the waves are in phase and constructive interference will occur otherwise they will be out of phase and would interfere destructively and cancel each other.

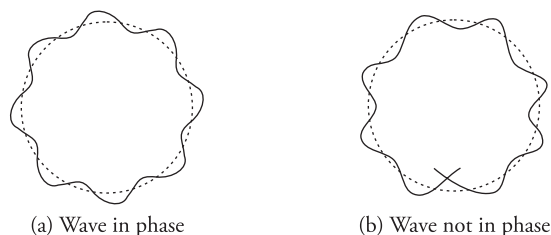


Figure 10.2 Constructive and destructive interference in a wave

Hence,

$$\text{Circumference} = n\lambda$$

$$2\pi r = n\lambda$$

However, according to de Broglie equation for an electron

$$\lambda = \frac{h}{mv}$$

$$\therefore 2\pi r = \frac{nh}{mv}$$

$$\text{or } mvr = \frac{nh}{2\pi}$$

Thus, angular momentum of an electron should be an integral multiple of $\frac{h}{2\pi}$. In other words, the angular momentum is quantised. This is nothing but the Bohr's postulate of quantisation of angular momentum.

Significance of de Broglie's relationship

de Broglie's equation is true for all material objects; however, it is significant for microscopic bodies only. Let us compare de Broglie's wavelength associated with bodies of

- (i) **Small mass** Let us consider an electron (mass 9.1×10^{-31} kg) moving with a velocity of 10^6 m s⁻¹.

de Broglie's wavelength is

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.11 \times 10^{-31} \text{ kg}) \times (10^6 \text{ m s}^{-1})}$$

$$= 7.28 \times 10^{-10} \text{ m}$$

The magnitude of this wavelength is of the same order as that X-ray, which can be easily measured.

- (ii) **Large mass** Consider a ball weighing 100 g (or 0.1 kg) and moving with the same velocity as that of electron (10^6 m s⁻¹). Its de Broglie wavelength is

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(0.1 \text{ kg}) \times (10^6 \text{ m s}^{-1})} = 6.63 \times 10^{-39} \text{ m}$$

This wavelength is shorter than the wavelength of any electromagnetic radiation and hence cannot be measured by any known method.

By the above discussion, it can be concluded that de Broglie's relation has no significance in daily life, as in daily life we come across large (macroscopic) objects that, although associated with wave, cannot be measured because their wavelengths are too small.

Solved Examples

1. Calculate the de Broglie's wavelength of an electron (mass = 9.1×10^{-31} kg) moving at velocity 1% the speed of light ($h = 6.63 \times 10^{-34}$ kg m² s⁻¹).

Solution

We know that $\lambda = \frac{h}{mv}$

$$m = 9.1 \times 10^{-31} \text{ kg} \quad h = 6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$v = 1\% \text{ speed of light} = \frac{1 \times 3.0 \times 10^8}{100} \text{ m s}^{-1} = 3.0 \times 10^6 \text{ m s}^{-1}$$

$$(\because \text{speed of light} = 3.0 \times 10^8 \text{ m s}^{-1})$$

$$\lambda = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (3.0 \times 10^6 \text{ m s}^{-1})} = 2.43 \times 10^{-10} \text{ m}$$

2. The kinetic energy of an electron is 4.55×10^{-25} J. Calculate its wavelength ($h = 6.6 \times 10^{-34}$ kg m² s⁻¹ and mass of electron = 9.1×10^{-31} kg).

Solution

Kinetic energy of electron =

$$\frac{1}{2} mv^2 = 4.55 \times 10^{-25} \text{ J} = 4.55 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}$$

$$v^2 = \frac{2 \times 4.55 \times 10^{-25} \text{ kg m}^2 \text{ s}^{-2}}{9.1 \times 10^{-31} \text{ kg}} = 1.0 \times 10^6 \text{ m}^2 \text{ s}^{-2}$$

$$v = \sqrt{1.0 \times 10^6} = 1 \times 10^3 \text{ m s}^{-1}$$

$$\text{Now, } \lambda = \frac{h}{mv} = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (1 \times 10^3 \text{ m s}^{-1})}$$

$$= 7.25 \times 10^{-7} \text{ m} = 725 \text{ nm}$$

3. Find out the de Broglie's wavelength of an alpha particle having a kinetic energy of 10 MeV ($h = 6.63 \times 10^{-34}$ J s, $1 \text{ MeV} = 1.602 \times 10^{-16}$ kJ).

Solution

Kinetic energy associated with alpha particle is

$$\begin{aligned}\frac{1}{2}mv^2 &= 10 \text{ MeV} = 10 \times 1.602 \times 10^{-16} \text{ kJ} \\ &= 1.602 \times 10^{-15} \text{ kJ}\end{aligned}$$

As α particles are helium nuclei (He^{2+}), the mass of α particle may be taken as that of the atom. Therefore, mass of α particle

$$= \frac{4.0}{6.023 \times 10^{23}} = 6.64 \times 10^{-24} \text{ g} = 6.64 \times 10^{-27} \text{ kg}$$

$$\text{Now, } \frac{1}{2}mv^2 = 1.602 \times 10^{-15} \text{ kJ} = 1.602 \times 10^{-12} \text{ J}$$

$$\frac{1}{2}mv^2 = 1.602 \times 10^{-12} \text{ kg m}^2 \text{ s}^{-2} \quad (\text{J} = \text{kg m}^2 \text{ s}^{-2})$$

$$v^2 = \frac{2 \times 1.602 \times 10^{-12} \text{ kg m}^2 \text{ s}^{-2}}{6.64 \times 10^{-27} \text{ kg}} = 4.825 \times 10^{14} \text{ m}^2 \text{ s}^{-2}$$

$$v = \sqrt{4.825 \times 10^{14} \text{ m}^2 \text{ s}^{-2}} = 2.20 \times 10^7 \text{ m s}^{-1}$$

Now de Broglie's wavelength

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(6.64 \times 10^{-27} \text{ kg}) \times (2.20 \times 10^7 \text{ m s}^{-1})} = 4.53 \times 10^{-15} \text{ m}$$

Practice Problems

- The de Broglie's wavelength of a particle is 0.1 nm. Find out its momentum. ($h = 6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$) [Ans $6.63 \times 10^{-24} \text{ kg m s}^{-1}$]
- A photon of sodium light of wavelength 5894 Å is moving with a velocity of $3 \times 10^8 \text{ m s}^{-1}$. Calculate its mass. ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$) [Ans $m = 3.74 \times 10^{-36} \text{ kg}$]
- Determine the ratio between the wavelength of an electron and a proton if the proton is moving with half the velocity of the electron (mass of proton = $1.67 \times 10^{-24} \text{ g}$ and mass of electron = $9.11 \times 10^{-28} \text{ g}$) [Ans $\lambda_{\text{electron}} / \lambda_{\text{proton}} = 916$]

10.4 Heisenberg's Uncertainty Principle

In our day-to-day life, we come across large objects; hence, it is possible to determine both the velocity and position accurately. However, in case of moving small particles (e.g., electron) we can never measure both the velocity and position accurately simultaneously. Werner Heisenberg (1927) put forward this fact in the form of *Heisenberg's uncertainty principle*. It states that

It is not possible to determine accurately the position and velocity (or momentum) of a microscopic particle.

Mathematical Expression It Δx and Δp are the uncertainties (or errors) in the measurements of position and momentum, respectively, of a particle then,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad (\text{i})$$

Thus expression is known as the *uncertainty relation*. The expression can be written as

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi} \quad (\text{ii})$$

where h is Planck's constant (6.625×10^{-34} J s or $\text{kg m}^2 \text{s}^{-1}$)

m = mass of the microscopic particle.

Δv = uncertainty in velocity.

Δx = uncertainty in position.

In expression (ii), the product of uncertainty in position and uncertainty in velocity is constant. It means that

If the position is measured accurately, that is, Δx is small then Δp will be large, that is, the momentum of the particle will not be determined accurately.

On the other hand, if Δp is small, that is, the momentum is measured accurately then Δx will be large and there will be uncertainty in the position of the particle.

In other words, *if the position of a particle is measured accurately, then momentum will not be determined accurately and vice versa.*

Why is accurate determination of position and momentum not possible simultaneously?

The position of an object can be determined only when we see it. For this, a light beam (photons) is thrown on the object. A part of this beam is scattered and the reflected part reaches the eye and makes the object visible. When a light beam falls on large objects their position and velocity is not affected by the impact of the beam of light. Hence, their positions and velocities can be determined accurately.

However, when the photon of light strikes a microscopic object, it displaces that object from its normal path. As a result, the particle undergoes considerable change in its path and velocity (or momentum) because of the impact of the photon used to view it.

If we wish to determine the position of the particle accurately, we need to take light of shorter wavelength. Shorter the wavelength larger is the frequency or larger is its energy. If a photon of small wavelength or large energy strikes an electron, the position will be measured accurately but a large momentum will be transferred to the electron and hence accurate determination of velocity or momentum will not be possible.

On the other hand, in order to minimize the change in momentum, if we use light of larger wavelength then the uncertainty in position will be large.

(According to the principle of optics, the accuracy in measurement of position of the particle depends upon the wavelength λ . In other words, the uncertainty in position is $\pm \lambda$).

Solved Examples

1. An electron is moving with a speed of 600 m s^{-1} . Its velocity is measured with an accuracy of 0.005%. Find the minimum error in measuring its position? (mass of electron = $9.1 \times 10^{-31} \text{ kg}$ and Planck's constant $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$)

Solution

$$\text{Here, } m = 9.1 \times 10^{-31} \text{ kg} \quad \Delta v = 600 \times .005\%$$

$$= \frac{600 \times .005}{100} = 0.03 \text{ m s}^{-1}$$

According to the uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \geq \frac{h}{4\pi m(\Delta v)} = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ kg} \times 0.03 \text{ m s}^{-1}}$$

$$\Delta x \geq 1.92 \times 10^{-3} \text{ m}$$

2. If an electron has a mass of $9.11 \times 10^{-31} \text{ kg}$ and the uncertainty in measuring its position is of the order of $\pm 10 \text{ pm}$, find the uncertainty in its velocity ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$).

Solution

Uncertainty in position

$$\Delta x = 10 \text{ pm} = 10 \times 10^{-12} \text{ m} = 10^{-11} \text{ m} \quad (\because 1 \text{ pm} = 10^{-12} \text{ m})$$

$$m = 9.11 \times 10^{-31} \text{ kg}, h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times m \Delta v \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi m \Delta x}$$

$$\Delta v \geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times \frac{22}{7} \times (9.11 \times 10^{-31} \text{ kg}) \times 10^{-11} \text{ m}} = 5.76 \times 10^6 \text{ m s}^{-1}$$

$$\Delta v \geq \pm 5.76 \times 10^6 \text{ m s}^{-1}$$

3. The mass of an electron is $9.1 \times 10^{-31} \text{ kg}$. Calculate the product of uncertainties in displacement and velocity if $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$.

Solution

According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times m \Delta v \geq \frac{h}{4\pi} \quad \text{or} \quad \Delta x \times \Delta v \geq \frac{h}{4m\pi}$$

$$m = 9.1 \times 10^{-31} \text{ kg}, h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1} \quad \pi = \frac{22}{7}$$

$$\Delta x \times \Delta v \geq \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times (9.1 \times 10^{-31} \text{ kg}) \times \frac{22}{7}}$$

$$\Delta x \times \Delta v \geq 5.77 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

Thus, the product of uncertainty in position and velocity of an electron is equal to or greater than $5.77 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$

Practice Problems

- The uncertainty in the position and velocity of a particle are $9.54 \times 10^{-10} \text{ m}$ and $5.5 \times 10^{-20} \text{ m s}^{-1}$, respectively. Calculate the mass of the particle ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$).
[Ans 10^{-6} kg]
- Calculate the uncertainty in the position of an electron if uncertainty in its velocity is (i) 0.001%, (ii) Zero (given mass of electron = $9.1 \times 10^{-31} \text{ kg}$, velocity of electron = 300 m s^{-1})
[Ans (i) $1.92 \times 10^{-2} \text{ m}$, (ii) infinity]

Uncertainty Principle and Bohr's theory—Probability Picture of Electrons and Concept of Atomic Orbital

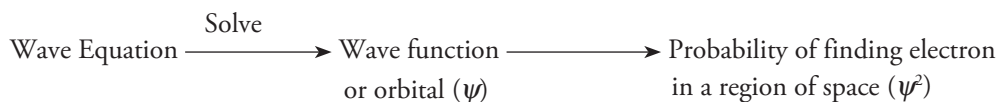
Bohr postulated that the electrons move in well-defined orbits with fixed velocity or energy. However, Heisenberg's uncertainty principle states that as an electron has a wave-like nature, simultaneous accurate determination of position and velocity is not possible. Hence, on the basis

of this principle, the Bohr's concept of stationary orbits is no longer correct. We can say that we can only predict the probability of finding (or locating) an electron with a probable velocity and energy in a given region of space at a given time. The uncertainty principle, which is based on the wave nature of the electron, gives the probability of finding the electron in a given space. It is for this reason that the old classical concept of Bohr has now been discarded in favor of the probability approach.

If ψ (Greek letter psi) gives the amplitude of the wave, then the square of ψ (i.e., ψ^2) gives the probability of finding an electron in a given region around the nucleus. Hence, we can identify the region of space around the nucleus where there is a higher probability of finding an electron. This space is called an atomic orbital. Thus,

Atomic orbital is defined as a three-dimensional region or space around the nucleus where there is higher probability of finding an electron having a certain energy.

This approach is called the quantum mechanical approach or wave mechanics. This approach helps in describing the position and energy levels of an electron with the help of wave functions.



The motion of macroscopic objects could be explained by the classical theory which failed to explain the behavior of microscopic particles (electrons, nuclei, atoms, molecules, photons etc.). Erwin Schrodinger developed quantum mechanical or wave mechanical model to explain the behavior of microscopic particles. The basis of his theory was de Broglie's idea of dual nature of matter and Heisenberg's uncertainty principle.

It is popularly known as the Schrodinger wave equation.

10.5 Schrodinger Wave Equation

The fundamental equation describing the behavior of a small particle in terms of wave motion is

$$\frac{d^2 \psi}{dx^2} = -\frac{4\pi^2 \psi}{\lambda^2}$$

$$\text{or } \frac{1}{\lambda^2} = -\frac{d^2 \psi}{dx^2} \times \frac{1}{4\pi^2 \psi} \quad (1)$$

where ψ = amplitude of the wave, x = displacement in a given direction and λ = wavelength. According to de Broglie's equation,

$$\lambda = \frac{h}{mv} \quad \text{or} \quad \frac{1}{\lambda^2} = \frac{m^2 v^2}{h^2} \quad (2)$$

where m = mass of particle, v = velocity of the particle and h = Planck's constant.

Comparing equations (1) and (2), we get

$$\frac{m^2 v^2}{h^2} = -\frac{d^2 \psi}{dx^2} \times \frac{1}{4\pi^2 \psi}$$

or $m^2 v^2 = -\frac{h^2}{4\pi^2 \psi} \times \frac{d^2 \psi}{dx^2}$ (3)

Now, for a particle of mass m moving with velocity v , the kinetic energy is given by $K = \frac{1}{2} mv^2$

or, $K = \frac{m^2 v^2}{2m}$

or $m^2 v^2 = K \times 2m$ (4)

Comparing (3) and (4)

$$K \times 2m = -\frac{h^2}{4\pi^2 \psi} \times \frac{d^2 \psi}{dx^2}$$

or, $K = -\frac{h^2}{8\pi^2 \psi m} \times \frac{d^2 \psi}{dx^2}$

Now the sum of kinetic energy K and potential energy V is the total energy E

$$E = K + V$$

Thus,

$$E = -\frac{h^2}{8\pi^2 \psi m} \times \frac{d^2 \psi}{dx^2} + V$$

or $\frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$ (5)

This equation is **Schrödinger's wave equation**. The above equation is in one dimension, along the x -axis. If written for a particle whose motion is described by three space coordinates x , y and z , then the above equation becomes

$$\frac{d^2 \psi}{dx^2} + \frac{d^2 \psi}{dy^2} + \frac{d^2 \psi}{dz^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$
 (6)

ψ (psi) is the amplitude of the wave, called wave function and $\frac{d^2 \psi}{dx^2}$ represents the second derivative of ψ with respect to x and so on. Being a differential equation of second order, the Schrodinger equation has several solutions for ψ but only those ψ values are acceptable and have significance

which correspond to some definite value of total energy E . Such permitted values of total energy are called *eigen values*. These values are also termed as *proper values* or *characteristic values*. Eigen function or wave function is the corresponding value of the function ψ . Each permitted solution (called eigen function) corresponds to a definite energy state of electrons and is known as the orbital. The electrons in an atom are present in atomic orbital and in a molecule are present in molecular orbital.

Interpretation of wave function:

The wave function ψ as such has no physical significance except that it represents the amplitude of the wave. ψ^2 has a physical meaning and gives the probability of finding an electron in a region of space. Since the region around the nucleus, which represents electron density, is the orbital, the wave function for an electron in an atom is called the *orbital wave function* or simply *atomic orbital*.

Normalised and orthogonal wave function:

A wave function is said to be normalised if it satisfies the condition,

$$\oint \psi \psi^* d\tau = 1 \quad (7)$$

where $\psi \psi^* d\tau$ is proportional to the probability of finding a particle in a small volume element $d\tau$. Integration over the whole configuration space gives the total probability of finding a particle in that space and it must be unity. \oint represents integration over the entire space and can also be

replaced by the symbol $\int_{-\infty}^{+\infty}$. Sometimes if the results of integration are not unity but are equal to some constant A , we have

$$\oint \psi \psi^* d\tau = A$$

To make the result equal to unity, we have

$$\frac{1}{A} \oint \psi \psi^* d\tau = 1$$

or
$$\oint \left(\frac{1}{A^{1/2}} \psi \right) \left(\frac{1}{A^{1/2}} \psi^* \right) d\tau = 1$$

The factor $\frac{1}{A^{1/2}}$ is the *normalised constant* and the function $\left(\frac{1}{A^{1/2}} \psi \right)$ is termed as the *normalised function*.

If ψ_a and ψ_b are two different eigen functions, then these functions are normalised if,

$$\oint \psi_a \psi_a^* d\tau = 1 \quad \text{and} \quad \oint \psi_b \psi_b^* d\tau = 1$$

They are said to be orthogonal if they satisfy the following conditions

$$\oint \psi_a \psi_b^* d\tau = 0 \quad \text{and} \quad \oint \psi_a^* \psi_b d\tau = 0 \quad (8)$$

If a wave function is both orthogonal and normalised it is called orthonormal.

Operators in Quantum Mechanics :

The concept of operator is very important in quantum mechanics. An operator is a mathematical instruction or procedure carried on a function so as to get another operator.

$$(\text{operator}).(\text{function}) = (\text{another function})$$

The commonly used operators are.

- (a) *Laplacian operator*: It is represented by ∇^2 (pronounced as 'del' squared) and is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (9)$$

The Schrodinger wave equation:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

may be written in terms of Laplacian operator as

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

- (b) *Hamiltonian operator*

The Schrodinger wave equation $\nabla^2 \psi + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$ may also be written as

$$\nabla^2 \psi = -\frac{8\pi^2 m}{h^2} (E - V) \psi$$

$$\text{or} \quad \nabla^2 \psi = -\frac{8\pi^2 m}{h^2} (E\psi - V\psi)$$

$$\text{or} \quad \frac{-h^2 \nabla^2 \psi}{8\pi^2 m} + V\psi = E\psi$$

$$\text{or} \quad \left[\frac{-h^2 \nabla^2}{8\pi^2 m} + V \right] \psi = E\psi \quad (10)$$

The term in parenthesis denotes the total energy multiplied with a function ψ . This term $\left[\frac{-h^2 \nabla^2}{8\pi^2 m} + V \right]$ is termed as the Hamiltonian operator and is represented as \hat{H}

Equation (10) may also be written as $\hat{H}\psi = E\psi$

This is a brief form of writing the Schrodinger wave equation.

In the above equation ψ is the eigen function and E is called the eigen value. Hence equation $\hat{H}\psi = E\psi$ is also termed as the eigen value equation. Thus for Schrodinger wave equation we can write:

$$(\text{Energy operator}) (\text{Wave function}) = (\text{Energy}) (\text{Wave function})$$

10.6 Particle in a One Dimensional Box

A particle in one-dimensional box provides one of simplest applications of wave mechanics. It explains why the associated energies are quantised and is the application of Schrodinger wave equation to the translational motion of a particle like an electron, atom etc. It also applies to a simple system like conjugated polyenes (the simplest being butadiene) where π electrons are easily modelled to first approximation by an equation similar to that for a particle in one dimension.

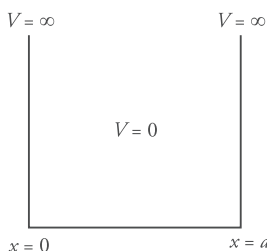


Figure 10.3 Particle in a box

Consider a particle which is restricted to move only along the x axis and is confined between $x = 0$ and $x = a$ by infinitely rigid walls. The particle bounces back and forth between the walls of the box and has no chance of penetrating it. Suppose the particle does not lose energy as it collides with the walls so that its total energy remains constant. This box can, then, be represented by a potential well or box of width 'a' with potential walls of infinite height at $x = 0$ and $x = a$, so that the potential energy V of the particle is infinite at both sides of the box and inside the box V is constant. For the sake of convenience we assume $V = 0$ inside the box (Fig. 10.3). For the particle to remain in the box it is essential to assume that the potential energy on or outside the wall is very high ($= \infty$) so that as soon as the particle reaches the walls, it is reflected back into the box and cannot escape from the box.

Schrodinger wave equation for one dimension is:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V)\psi = 0 \quad (1)$$

Here ψ has been taken as a function of x coordinate only. Outside the box $V = \infty$, hence equation (1) becomes:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - \infty)\psi = 0 \quad (2)$$

Neglecting E in comparison to ∞ , equation (2) reduces to

$$\begin{aligned} \frac{d^2\psi}{dx^2} - \infty\psi &= 0 \quad \left(\frac{8\pi^2m}{h^2} \times \infty = \infty \right) \\ \frac{d^2\psi}{dx^2} &= \infty\psi \\ \psi &= \frac{1}{\infty} \cdot \frac{d^2\psi}{dx^2} = 0 \end{aligned} \quad (3)$$

Equation (3) implies that outside the box $\psi = 0$ hence particle cannot go outside the box. As studied earlier, for the particle inside the box $V = 0$, the Schrodinger wave equation (1) becomes

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}E\psi = 0 \quad (4)$$

According to one of the postulates of quantum mechanics for a given state of the system energy E is constant. Thus:

$$\frac{8\pi^2m}{h^2}E = k^2 \quad (5)$$

where k^2 is a constant independent of x

Placing (5) in (4), we have

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad (6)$$

The solution of this differential equation is given by

$$\psi = A \sin kx + B \cos kx \quad (7)$$

where A and B are constants.

Although Ψ can have many values depending upon the value of A, B and k, only those values which satisfy the boundary conditions are acceptable, that is

$$\Psi = 0 \text{ at } x = 0$$

$$\Psi = 0 \text{ at } x = a$$

Putting $\Psi = 0$ at $x = 0$, equation (7) becomes

$$0 = A \sin 0 + B \cos 0$$

$$\therefore B = 0 \quad (\because \sin 0 = 0 \text{ and } \cos 0 = 1)$$

Thus putting the value of $B = 0$ in equation (7) under the boundary condition $x = 0$, we have

$$\Psi = A \sin kx \quad (8)$$

Now taking up the next condition

$\Psi = 0$ when $x = a$, equation (8) becomes

$$0 = A \sin ka$$

$$\text{that is, } \sin ka = 0 \quad (9)$$

The above equation holds good only when the values of ka are integral multiples of π , that is,

$$ka = n\pi \quad (10)$$

where n is an integer $n = 0, 1, 2, 3 \dots$. However $n = 0$ is not acceptable because it makes $k = 0$ and hence $\Psi = 0$ for any value between 0 and a , that is, within the box. This cannot be true as the particle is always assumed to be present within the box. From equation (10)

$$k = \frac{n\pi}{a} \quad (11)$$

Substituting the value in equation (8) we get

$$\Psi = A \sin\left(\frac{n\pi}{a} \cdot x\right) \quad (12)$$

This gives the expression for eigen function Ψ . The expression for eigen value for energy may be obtained as follows from equation (5)

$$E = \frac{k^2 \hbar^2}{8\pi^2 m} \quad (13)$$

Substituting the value of k from equation (11), we get

$$E = \frac{\left(\frac{n\pi}{a}\right)^2 h^2}{8\pi^2 m}$$

$$E = \frac{n^2 h^2}{8ma^2} \quad (14)$$

Equation (14) gives the energy of the particle. The integer n corresponding to energy E is called quantum number, which takes the value $n = 1, 2, 3, 4, \dots$. Thus energy of a particle in one dimensional box acquires discrete values. $E = 0$ is excluded, because if $E = 0$ inside the box, then Ψ becomes zero, which means that the particle no longer exists in the box which is wrong as there is no possibility of leakage of the particle from the box. Hence, E can have all values of energy excluding zero value

When $n = 1$

$$E_1 = \frac{h^2}{8ma^2}$$

When $n = 2$

$$E_2 = \frac{4h^2}{8ma^2} = 4E_1$$

When $n = 3$

$$E_3 = \frac{9h^2}{8ma^2} = 9E_1$$

When $n = 4$

$$E_4 = \frac{16h^2}{8ma^2} = 16E_1$$

Wave Function Inside a Box

The wave function of particle inside a box is given by

$$\Psi_{(x)} = A \sin \frac{n\pi x}{a}$$

To determine the coefficient A in the wave function the normalisation condition is applied.

Normalisation of Ψ : Since the probability of finding the particle within the box is 1

$$\int_0^a \Psi_x^2 dx = 1 \quad (\text{Born's interpretation of wave function})$$

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$$

This is an elementary integral equation which gives

$$A^2 \cdot \frac{a}{2} = 1, \text{ hence } A = \sqrt{\frac{2}{a}}$$

Thus the normalised wave function for the particle are

$$\psi_n(x) = \left(\frac{2}{a}\right)^{\frac{1}{2}} \sin \frac{n\pi x}{a}; n = 1, 2, 3, \dots$$

It may be noted that quantisation arises naturally from the boundary conditions. Figure 10.4 gives the wave function Ψ and the probability distribution function Ψ^2 for a particle in a box.

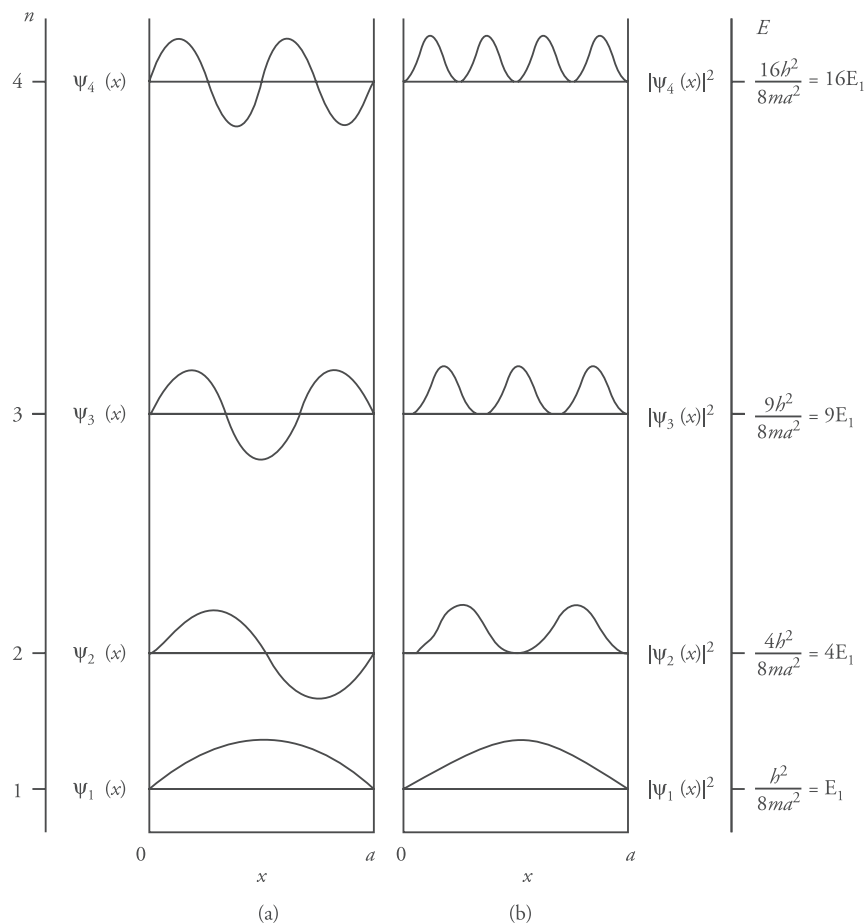


Figure 10.4 (a) The energy levels and wave functions
(b) probability densities for the particle in one dimensional box

From the figure it is clear that for $n = 1$ the most probable position for a particle is the centre of the box. It may be noted that when the energy levels are far apart quantisation is distinct. But as the value of ' a ' increases the energy levels get closer. If the box length become very large (or the very heavy particle) the energy levels come very close to each other and quantisation becomes unnoticeable and there is a smooth transition from quantum behaviour to classical behaviour (continuous change).

Solved examples

1. Calculate the ground state energy for an electron confined to a potential well (one-dimensional box) having width of 0.3 nm.

Solution:

The energy of a particle in one dimensional box is given by $E = \frac{n^2 h^2}{8ma^2}$

For ground state:

$$n = 1$$

$$\begin{aligned}\text{mass of electron } m &= 9.1 \times 10^{-31} \text{ kg} \\ a &= 0.3 \text{ nm} = 0.3 \times 10^{-9} \text{ m} \\ h &= 6.626 \times 10^{-34} \text{ Js}\end{aligned}$$

$$E = \frac{(1)^2 (6.626 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.3 \times 10^{-9})^2} = 6.7 \times 10^{-19} \text{ J}$$

Energy for one mole electrons

$$E = \frac{6.7 \times 10^{-19} \times 6.023 \times 10^{23}}{10^3} \text{ kJ mol}^{-1} = 403.5 \text{ kJ mol}^{-1}$$

2. Calculate the energy (in eV) of an electron in third energy level confined to one-dimensional box of width 3 Å.

Solution:

For a one dimension box $E = \frac{n^2 h^2}{8ma^2}$

$$n = 3, m = 9.1 \times 10^{-31} \text{ kg}, a = 3 \times 10^{-10} \text{ m}, h = 6.626 \times 10^{-34} \text{ Js}$$

$$E = \frac{(3)^2 (6.626 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (3 \times 10^{-10})^2} = 6.03 \times 10^{-18} \text{ J}$$

$$\therefore 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$E = \frac{6.03 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV} = 37.68 \text{ eV} \quad (1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

3. Prove that the wave function of a particle in a one dimensional box of width 'a' and infinite height are orthogonal.

Solution:

$$\psi_{n(x)} = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}; n = 1, 2, 3, \dots$$

A wave function is orthogonal if it satisfies the condition

$$\int_0^a \psi_m^*(x) \psi_n(x) dx = 0$$

Since the wave functions are real

$$\psi_m^*(x) = \psi_m(x) = \sqrt{\frac{2}{a}} \sin \frac{m\pi x}{a}$$

Hence,

$$\begin{aligned} \int_0^a \psi_m^* \psi_n dx &= \int_0^a \sqrt{\frac{2}{a}} \sin \frac{m\pi x}{a} \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} dx \\ &= \frac{2}{a} \int_0^a \sin \frac{m\pi x}{a} \sin \frac{n\pi x}{a} dx \end{aligned}$$

$$\text{since } \sin A \sin B = \frac{1}{2} [\cos(A - B) - \cos(A + B)]$$

The above equation can be written as

$$\begin{aligned} \int_0^a \psi_m^* \psi_n dx &= \frac{1}{a} \int_0^a [\cos(m - n) \frac{\pi x}{a} - \cos(m + n) \frac{\pi x}{a}] dx \\ &= \frac{1}{a} \left[\frac{a}{(m - n)\pi} \sin \left[(m - n) \frac{\pi x}{a} \right]_0^a - \frac{a}{(m + n)\pi} \sin \left[(m + n) \frac{\pi x}{a} \right]_0^a \right] = 0 \\ &\quad (m \text{ and } n \text{ are integers}) \end{aligned}$$

Hence verified

10.7 Particle in a Three Dimensional Box

Let us now consider a particle of mass 'm' confined to a three dimensional cubical box with length of the edges 'a' and volume a^3 . As assumed earlier the potential energy of the particle inside the box is constant (taken as equal to zero) and is infinite (∞) on the walls (i.e., at the boundaries) and outside the box.

The Schrodinger wave equation for a particle in a three dimensional box is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad (15)$$

where E represents the total energy of the particle. V is the potential energy and Ψ is the function of three coordinates x , y and z . For a particle within the box $V = 0$, hence equation (15) takes the form

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E \Psi = 0 \quad (16)$$

The above equation can be solved by separating the variables. For this purpose Ψ , which is a function of x , y and z is taken as equal to the product of three function $X_{(x)}$, $Y_{(y)}$, and $Z_{(z)}$ each in one variable, that is

$$\Psi(x, y, z) = X_{(x)} Y_{(y)} Z_{(z)} \quad (17)$$

For the sake of simplicity, we may write it as

$$\Psi = XYZ \quad (18)$$

Substituting the value of Ψ in equation (16), we get

$$\frac{\partial^2 (XYZ)}{\partial x^2} + \frac{\partial^2 (XYZ)}{\partial y^2} + \frac{\partial^2 (XYZ)}{\partial z^2} + \frac{8\pi^2 m}{h^2} E (XYZ) = 0$$

$$YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E (XYZ) = 0$$

Dividing throughout by XYZ , we get

$$\begin{aligned} \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E &= 0 \\ \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} &= -\frac{8\pi^2 m}{h^2} E \end{aligned} \quad (19)$$

The total energy E of the particle is constant. Therefore, the RHS of equation (19) is constant and we may put

$$\frac{8\pi^2 m}{h^2} E = k^2$$

Hence equation (19) may be written as

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -k^2 \quad (20)$$

The sum of the three terms is constant. We notice from the above equation that the first term is a function of x only and is independent of y and z . The second term is a function of y only and is independent of x and z , whereas the third term is a function of z only and is independent of x and y .

∴ the sum of the three terms is constant, hence each of these terms of LHS of equation (20) must be a constant and their sum must be equal to k^2 .

Hence we may write

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -k_x^2 \quad (21a)$$

$$\frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} = -k_y^2 \quad (21b)$$

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -k_z^2 \quad (21c)$$

where k_x^2, k_y^2 and k_z^2 are constant such that

$$k_x^2 + k_y^2 + k_z^2 = k^2 \quad (22)$$

The value of these constants is as follows

$$k_x^2 = \frac{8\pi^2 m}{h^2} E_x \quad (23a)$$

$$k_y^2 = \frac{8\pi^2 m}{h^2} E_y \quad (23b)$$

$$k_z^2 = \frac{8\pi^2 m}{h^2} E_z \quad (23c)$$

where E_x, E_y and E_z represent the component of energy parallel to the x -axis, y -axis and z -axis, respectively, and

$$E = E_x + E_y + E_z \quad (24)$$

Equation (21 a-c) may be rewritten as

$$\frac{\partial^2 X}{\partial x^2} + k^2 X = 0, \quad \frac{\partial^2 Y}{\partial y^2} + k^2 Y = 0, \quad \frac{\partial^2 Z}{\partial z^2} + k^2 Z = 0$$

Each of these equations is of the same form as for the particle in one dimensional box. The solution of which is given by

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} \cdot x; \quad n_x = 1, 2, 3$$

$$\text{and } E_x = \frac{n_x^2 h^2}{8ma^2} \quad (25a)$$

Similar solutions exist for Y (y) and Z (z), that is

$$Y(y) = \sqrt{\frac{2}{a}} \sin \frac{n_y \pi}{a} \cdot y \quad E_y = \frac{n_y^2 h^2}{8ma^2} \quad (25b)$$

$$\text{and } Z(z) = \sqrt{\frac{2}{a}} \sin \frac{n_z \pi}{a} \cdot z \quad E_z = \frac{n_z^2 h^2}{8ma^2} \quad (25c)$$

where n_x , n_y and n_z have integral values 1, 2, 3 which represent three quantum numbers parallel to the three axis. Now,

$$\begin{aligned} \psi(x, y, z) &= X_{(x)} Y_{(y)} Z_{(z)} \\ &= \left[\sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} \cdot x \right] \left[\sqrt{\frac{2}{a}} \sin \frac{n_y \pi}{a} \cdot y \right] \left[\sqrt{\frac{2}{a}} \sin \frac{n_z \pi}{a} \cdot z \right] \\ &= \sqrt{\frac{8}{a^3}} \left[\sin \frac{n_x \pi x}{a} \right] \left[\sin \frac{n_y \pi y}{a} \right] \left[\sin \frac{n_z \pi z}{a} \right] \end{aligned} \quad (26)$$

Total energy $E = E_x + E_y + E_z$

$$= \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8ma^2} \quad (27)$$

where $n_x, n_y, n_z = 1, 2, 3, 4, \dots$

Equation (27) is the expression for the energy of a particle in a three dimensional cubical box.

10.8 Schrodinger Wave Equation for Hydrogen and Hydrogen-Like System

The application of Schrodinger wave equation to hydrogen and hydrogen like atoms is very important for chemists as it is the only realistic system that can be solved analytically using the Schrodinger wave equation. A hydrogen like atom can have two types of motion, the revolution of electron around the nucleus and the translational motion of the nucleus. Assuming that the nucleus is stationary, only the revolution of electron around nucleus is considered, E will represent the electronic energy. The Schrodinger wave equation for hydrogen like atom is written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

where 'm' is the mass of the particle, E is its total energy, V is its potential energy and x, y and z are the coordinates of the particle. The above equation is applicable for the motion of a single particle.

For hydrogen like particles, the electron is moving under the central field of the nucleus. Hence, if $-e$ is the charge on the electron and $+Ze$ is the charge on the nucleus (Z being the atomic number of the element) and r is the distance between the electron and the nucleus, the potential energy V is given by

$$V = \frac{-Ze^2}{r} \quad (29)$$

Thus putting the value of potential energy in the Schrodinger wave equation we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{Ze^2}{r} \right) \psi = 0 \quad (30)$$

The above equation is expressed in terms of cartesian coordinates taking the nucleus as the origin and hence the position of electron is defined by the coordinates x , y and z . Since an atom has a spherical symmetry hence cartesian coordinates cannot express its position, so it is better to use polar coordinates to solve the Schrodinger wave equation. Hence the above equation is expressed in terms of spherical polar coordinates (r , θ , ϕ). The relation between the two systems is shown in Figure 10.5.

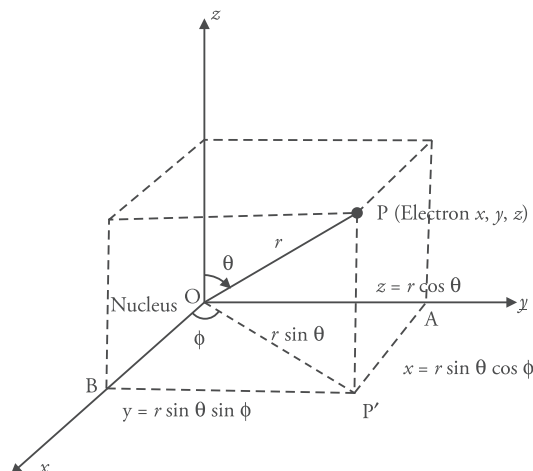


Figure 10.5 Relation between cartesian coordinates (x , y , z) and spherical polar coordinates (r , θ , ϕ)

The use of polar coordinates is analogous to the method used to specify the position on the earth's surface when the position of a point is defined by the radius of the earth and by two angles: the latitude and the longitude.

The value of θ at any point P (electron) is then described by polar coordinates (r , θ , ϕ). In Figure 10.5,

- r is the radial distance (called radius vector or radial line) of point P (electron) from the origin O (nucleus). Expressing r in terms of x , y and z

$$r = \sqrt{x^2 + y^2 + z^2}$$

- θ is the angle between the radius vector OP and +z axis (i.e., OZ axis), which is the axis of the sphere. This angle called the zenith angle is given by

$$\theta = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

- Drop a perpendicular PP' from P on the xy-plane such that OP' makes an angle ϕ with +x axis (i.e., OX axis), measured in the direction shown. This angle called the azimuthal angle or longitudinal angle is given by

$$\phi = \tan^{-1} \frac{y}{x}$$

P'A and P'B are the normals drawn from P' on OY and OX-axis, respectively.

From Figure 10.5, the spherical polar coordinates are

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned} \quad (31)$$

where $r = 0$ to ∞ , $\theta = 0$ to π and $\phi = 0$ to 2π .

On substituting the above relation in equation (30), the Schrodinger wave equation for hydrogen-like particles in terms of spherical coordinates can be written as

$$\frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] + \frac{8\pi^2 m}{h^2} \left(E + \frac{Ze^2}{r} \right) \psi = 0 \quad (32)$$

Separation of Variables:

In equation (32), the wave function Ψ is a function of three variables, r , θ , ϕ and Ψ can therefore be separated into the product of three function, $R(r)$, $\Theta(\theta)$ and $\Phi(\phi)$. The solution of equation (32), that is, evaluation of $\Psi(r, \theta, \phi)$ is possible only if the function Ψ can be written in the form

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (33)$$

Here by writing $R(r)$ we mean that the function R depends on ' r ' only and is independent of θ and ϕ , $\Theta(\theta)$ is a function dependent on θ only and is independent of r and ϕ , and $\Phi(\phi)$ is a function of ϕ and is independent of r and θ .

The function $R(r)$ is known as the *radial wave function* while the function $\Theta(\theta)$ and $\Phi(\phi)$ are called *angular wave function*.

For the sake of simplicity equation (33) may be written as

$$\psi = R.\Theta.\Phi \quad (34)$$

And correspondingly

$$\begin{aligned}\frac{d\psi}{dr} &= \Theta\Phi \frac{dR}{dr} \\ \frac{d\psi}{d\theta} &= R\Phi \frac{d\Theta}{d\theta} \\ \frac{d\psi}{d\phi} &= R\Theta \frac{d\Phi}{d\phi}\end{aligned}\quad (35)$$

Substituting the value of equations (34) and (35) in equation (32) we get

$$\frac{1}{r^2} \left[\Theta\Phi \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R\Phi}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{R\Theta}{\sin^2\theta} \frac{d^2\Phi}{d\phi^2} \right] + \frac{8\pi^2 m}{h^2} \left(E + \frac{Ze^2}{r} \right) R\Theta\Phi = 0 \quad (36)$$

Multiplying throughout by r^2 and dividing by $R\Theta\Phi$ we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi \sin^2\theta} \frac{d^2\Phi}{d\phi^2} + \frac{8\pi^2 m r^2}{h^2} \left(E + \frac{Ze^2}{r} \right) = 0 \quad (37)$$

Separating the radial variable (r) and angular variables θ and ϕ we get

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 m r^2}{h^2} \left(E + \frac{Ze^2}{r} \right) = -\frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) - \frac{1}{\Phi \sin^2\theta} \frac{d^2\Phi}{d\phi^2} \quad (38)$$

As r , θ , ϕ are independent variables equation (38) holds good if each side is equal to the same constant say β thus

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{8\pi^2 m r^2}{h^2} \left(E + \frac{Ze^2}{r} \right) = \beta \quad \text{Radial equation} \quad (39)$$

$$\text{and} \quad \frac{1}{\Theta \sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi \sin^2\theta} \frac{d^2\Phi}{d\phi^2} = -\beta \quad \text{Angular equation} \quad (40)$$

The terms θ and ϕ can be further separated by multiplying equation (40) by $\sin^2\theta$ throughout, thus

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} = -\beta \sin^2\theta$$

$$\text{or} \quad \frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2\theta = -\frac{1}{\Phi} \frac{d^2\Phi}{d\phi^2} \quad (41)$$

Equation (41) holds good if each side is equal to a constant. Let m^2 be the constant, then

$$\frac{\sin\theta}{\Theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2\theta = m^2 \quad (42)$$

and
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (43)$$

Thus the Schrodinger wave equation has been separated into three equations (41), (42) and (43) in r , θ and ϕ , respectively.

The radial wave function $R(r)$ gives the *energy and size of the orbitals* and the angular wave function which is a product of $\Theta(\theta)$ and $\Phi(\phi)$ gives the shapes of the orbitals. These aspects have been discussed below:

1. **Radial Wave Function $R(r)$:** The solution of equation (39) for hydrogen and hydrogen like atoms yields two quantum numbers n and l . The quantum number n is analogous to the principal quantum number of the Bohr's theory and can have integral value 1, 2, 3 ... etc. The quantum number l can have values from 0 to $n-1$ and it is analogous to the azimuthal quantum number of the Bohr- Sommerfeld theory. The variable l are given special designation s, p, d, f for $l = 0, 1, 2, 3$ respectively.

The radial wave functions are generally written as $R_{n,l}(r)$ or simply $R_{n,l}$ for the sake of simplicity.

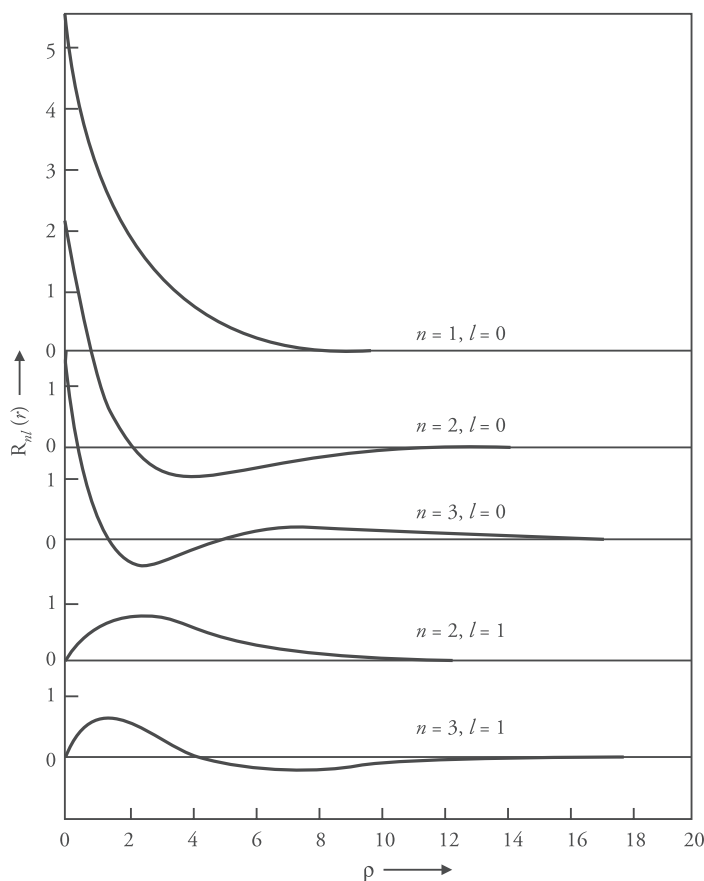


Figure 10.6 Hydrogen-atom radial wave functions $R_{n,l}(r)$ for $n = 1, 2$, and 3 and $l = 0$ and 1

The radial wave function for electrons present in different s and p orbitals are given below

$$n = 1 \quad l = 0 \quad R_{1,0} = 2 \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$$

(Represents radial wave function of electron in 1s orbitals)

$$n = 2 \quad l = 0 \quad R_{2,0} = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}$$

(Represents radial wave function of electron in 2s orbitals)

$$n = 2 \quad l = 1 \quad R_{2,1} = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}}$$

(Represents radial wave function of electron in 2p orbital)

In the above functions a_0 is the Bohr's radius and Z is the atomic number.

The plots of radial wave function for hydrogen atom are given in Figure 10.6.

2. **Angular wave function:** The angular wave function are obtained by the solution of theta phi (θ, ϕ) equation (equation 40)

Equation in the variable Φ (equation 43) is

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2$$

The solution of above equation to provide normalised eigen function is :

$$\phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad (44)$$

where $m = 0, \pm 1, \pm 2 \dots \dots \dots \pm l$.

Similarly, equation in the variable θ (equation 42) is

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta = m^2$$

Putting the value of β as $l(l+1)$ we get,

$$\Theta_{l|m} = \sqrt{\frac{2l+1(l-|m|)!}{2(l+|m|)!}} P_l^{|m|}(\cos \theta) \quad (45)$$

where $P_l^{|m|}$ represents associated Legendre polynomial of degree l and order m defined by the expression.

$$P_l^{|m|}(x) = (1-x^2)^{|m|/2} \frac{d^{|m|} P_l(x)}{d_x^{|m|}} \quad (46)$$

in which $P_l(x)$ is defined by the expression:

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l (x^2 - 1)^l}{dx^l} \quad (47)$$

The solution for angular equation (40) given by $\Theta\Phi$ is called spherical harmonics and its solution leads to two quantum numbers m and l . There are $2l + 1$ values of l for each value of l , solutions which are independent of r .

$$Y_l^m = (\theta, \phi)$$

A few spherical harmonics are given in Table 10.1.

Table 10.1 Spherical harmonics (angular wave function for hydrogen like atoms)

$l = 0$	$m = 0$	$Y_0^0 = \frac{1}{\sqrt{4\pi}}$
$l = 1$	$m = 0$	$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$
$l = 1$	$m = 1$	$Y_1^1 = -\sqrt{\frac{3}{8\pi}} (\sin \theta) e^{i\phi}$
$l = 1$	$m = -1$	$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} (\sin \theta) e^{-i\phi}$
$l = 2$	$m = 2$	$Y_2^2 = \sqrt{\frac{15}{32\pi}} (\sin^2 \theta) e^{2i\phi}$
$l = 2$	$m = 1$	$Y_2^1 = -\sqrt{\frac{15}{8\pi}} (\sin \theta \cos \theta) e^{i\phi}$
$l = 2$	$m = 0$	$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
$l = 2$	$m = -1$	$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} (\sin \theta \cos \theta) e^{-i\phi}$
$l = 2$	$m = -2$	$Y_2^{-2} = \sqrt{\frac{15}{32\pi}} (\sin^2 \theta) e^{-2i\phi}$

10.9 Huckel Molecular Orbital (HMO) Theory for Conjugate System

Unsaturated carbon compounds containing alternate double and single bonds are termed as conjugated molecules. The carbon atoms in such molecules is sp^2 hybridised and the three sp^2 hybrid orbitals lie in a plane called the molecular plane. These form bonds with the three neighbouring atoms, while the unhybridised $2p_z$ orbitals lies with its axis perpendicular to the molecular plane.

The $2p_z$ orbital which is perpendicular to the molecular plane contains one π electron. According to the LCAO approximation, the molecular orbital is written as

$$\psi = \sum_i C_i \phi_i \quad (1)$$

where ϕ_i is the $2p_z$ atomic orbital centered on carbon atom i and the summation represents all the $2p_z$ atomic orbitals. The coefficient and energies of these orbitals are obtained by solving equation

$$\sum_{i=1}^n C_i (H_{ij} - \delta_{ij} E) = 0 \quad (2)$$

$$j = 1, 2, 3, \dots, n$$

where, $H_{ij} = \langle \phi_i | H | \phi_j \rangle$

$$\delta_{ij} = \langle \phi_i | \phi_j \rangle \quad (3)$$

A set of secular equation (2) are obtained in accordance to the variation principle.

Huckel made a set of approximations:

1. All overlap integrals are zero, that is, $\delta_{ij} = 0$
2. The term $H_{ii} (= \langle \phi_i | H | \phi_i \rangle)$, called *coulomb integral* refers to the energy of the electron in the $2p_z$ orbital on the i^{th} carbon atom. Since we are dealing with molecules containing carbon atoms only, all such integrals are equal and are denoted by the symbol α .
3. The term $H_{ij} (= \langle \phi_i | H | \phi_j \rangle)$ is called *resonance integral or exchange integral*. They represent the energy of interaction of two atomic orbitals. If the atoms i and j are not directly bonded $H_{ij} = 0$ and if they are bonded directly H_{ij} is finite. All such integrals are assumed to be finite and are denoted by the symbol β .

The Huckel secular equation can now be written as

$$\begin{bmatrix} \alpha - E & \beta & 0 & 0 & 0 \\ \beta & \alpha - E & \beta & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & \beta & \alpha - E & \beta \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix} = 0 \quad (4)$$

Dividing the matrix by β we have :

$$\begin{bmatrix} \frac{\alpha - E}{\beta} & 1 & 0 & 0 & 0 \\ 1 & \frac{\alpha - E}{\beta} & 1 & 0 & 0 \\ 0 & 1 & \frac{\alpha - E}{\beta} & 1 & 0 \\ 0 & 0 & 1 & \frac{\alpha - E}{\beta} & 1 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix} = 0 \quad (5)$$

If $\frac{\alpha - E}{\beta} = x$, then the above matrix becomes

$$\begin{bmatrix} x & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix} = 0 \quad (5)$$

The expansion on an $n \times n$ determinant yields a polynomial equation having n real roots: thus the conjugated polymer has n energy levels and n MOs. The energy of the k^{th} MO is given by

$$E_k = \alpha - x_k \beta \quad (6)$$

where x_k is the k^{th} root of the polynomial. Since both α (coulomb integral) and β (resonance integral) are negative, a positive value of x_k represents an energy level which is more negative and hence more stable than the energy of an electron in a carbon $2p_z$ orbital. This energy level is called the bonding molecular orbital (BMO). Similarly a negative value of x_k represents an orbital having higher energy and hence lesser stability than an electron in the $2p_z$ orbital. This level is termed as the antibonding molecular orbital (ABMO). The energy level corresponding to $x_k = 0$ is called the nonbonding molecular orbital.

We shall now briefly discuss the applications of HMO to ethylene, 1,3-butadiene and benzene.

Ethylene:

Although ethylene is not a conjugate system but it is of interest being the simplest molecule to study the application of HMO.

An ethylene molecule has two carbon atoms in sp^2 hybridised state and the two p orbital containing one π electron each are perpendicular to the plane of carbon atom. Let the two p orbitals be represented by ϕ_1 and ϕ_2 then

$$\psi = c_1 \phi_1 + c_2 \phi_2 \quad (7)$$

The Huckel secular equation will be a two by two matrix

$$\begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (8)$$

Expanding the determinant of the matrix we get

$$x^2 - 1 = 0 \quad \text{or} \quad x = \pm 1$$

$$\text{where } x = \frac{\alpha - E}{\beta}$$

$$\text{If } x = -1 \quad \text{then} \quad E_1 = \alpha + \beta \text{ (BMO)} \quad (9)$$

$$x = +1 \quad \text{then} \quad E_2 = \alpha - \beta \text{ (ABMO)} \quad (10)$$

The two π electrons of ethylene occupy the BMO (Fig. 10.7) in the ground state in accordance with the Pauli's exclusion principle.

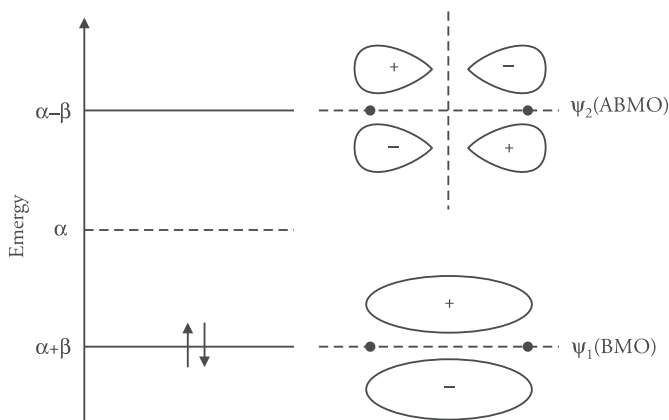


Figure 10.7 HMO diagram of ethylene. The carbon atoms are represented by dots and the nodal planes for the MOs are represented by dashed lines

To determine the BMO ψ_1 and anti-bonding molecular orbital ψ_2 we proceed as follows:
If $x = -1$ then the matrix equation (8) becomes

$$\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \quad (11)$$

On multiplying we get

$$-c_1 + c_2 = 0 \quad \text{and} \quad c_1 - c_2 = 0 \quad \text{or} \quad c_1 = c_2$$

Hence the expression for the corresponding MO

$$\begin{aligned} \psi_1 &= c_1\phi_1 + c_2\phi_2 & \because c_1 &= c_2 \\ \psi_1 &= c_1(\phi_1 + \phi_2) \end{aligned}$$

$\therefore \psi_1$ is normalised, that is,

$$\begin{aligned} \int \psi_1 \psi_1 d\tau &= 1 \quad \text{we have} \\ \int c_1^2 (\phi_1^2 + \phi_2^2) d\tau &= c_1^2 \left(\int \phi_1^2 d\tau + \int \phi_2^2 d\tau + 2 \int \phi_1 \phi_2 d\tau \right) = 1 \end{aligned} \quad (12)$$

In the above equation ϕ_1 and ϕ_2 are normalised and the last term represents the overlap integral which is zero according to Huckels approximation. Hence

$$\int \phi_1^2 d\tau = \int \phi_2^2 d\tau = 1 \quad \text{and} \quad \int \phi_1 \phi_2 d\tau = 0$$

Substituting the value in equation (12) we get

$$c_1^2(1+1) = 1 \quad \text{or} \quad c_1 = \frac{1}{\sqrt{2}}$$

$$\text{Hence } \psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \text{ BMO} \quad (13)$$

Now if $x = +1$, then the Hückel secular equation (8) can be written as

$$\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

Solving as done previously we get $c_1 = -c_2$

Proceeding as above

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \text{ ABMO} \quad (14)$$

Now the total π electron energy E_π of ethene

$$E_\pi = 2(\alpha + \beta)$$

While calculating the above value, the electron-electron repulsion has been ignored. α and β are taken as experimentally determined parameters and the value of β is found to be 230 kJ/mol.

1,3-Butadiene:

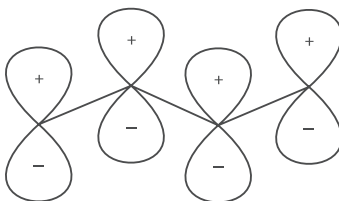


Figure 10.8 *p orbitals of butadiene*

Butadiene contains four π orbitals and four π electrons. The Hückel secular equation is

$$\begin{bmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \end{bmatrix} = 0$$

This determinant on expansion gives the following polynomial equation

$$x^4 - 3x^2 + 1 = 0 \quad (16)$$

which has the following roots

$$x = \pm 1.618, \pm 0.618 \quad (17)$$

The following energy levels are obtained

$$\begin{aligned} E_1 &= \alpha + 1.618\beta & (BMO) \\ E_2 &= \alpha + 0.618\beta & (BMO) \\ E_3 &= \alpha - 0.618\beta & (ABMO) \\ E_4 &= \alpha - 1.618\beta & (ABMO) \end{aligned} \quad (18)$$

Using the procedure employed in case of ethylene the four MOs (two BMOs and two ABMOs) can be obtained as follows

$$\psi_1 = 0.3755(\phi_1 + \phi_2) + 0.6070(\phi_2 + \phi_3) \quad (19)$$

$$\psi_2 = 0.6070(\phi_1 - \phi_4) + 0.3755(\phi_2 - \phi_3) \quad (20)$$

$$\psi_3 = 0.6070(\phi_1 + \phi_4) - 0.3755(\phi_2 + \phi_3) \quad (21)$$

$$\psi_4 = 0.3755(\phi_1 - \phi_4) - 0.6070(\phi_2 - \phi_3) \quad (22)$$

The schematic representation of these four molecular orbitals is shown in Figure 10.9.

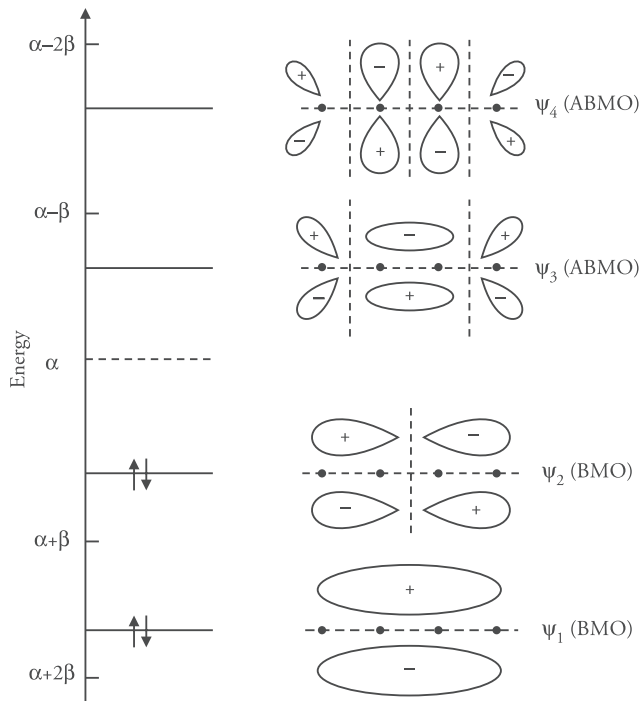


Figure 10.9 HMO diagram for 1,3-butadiene. The carbon atoms are represented by dots and the nodal planes for the MOs are represented by dashed lines.

As seen ψ_1 has no node, ψ_2 has one node, ψ_3 has two nodes and ψ_4 has three nodes.

The four π electrons in 1,3-butadiene occupy the two BMOs hence the total π electron energy E_π is equal to

$$[2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)] \quad \text{i.e., } 4\alpha + 4.472\beta$$

Butadiene has the following classical structure $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, that is, it has two ethene like double bonds. If butadiene has the above structure its π electron energy would be $4(\alpha + \beta)$ as the E_π of one ethylene molecule is $2(\alpha + \beta)$ as discussed earlier. But actually the energy is $4\alpha + 4.472\beta$. Hence the energy of butadiene is $[4\alpha + 4.472\beta - 2(2\alpha + 2\beta)] = 0.472\beta$ lower than that of ethylene. This is the delocalisation energy (DE) or the resonance energy (RE) which is approximately 110 kJ/mol. Thus butadiene is more stable than two ethylene molecules by energy of 0.472β .

Benzene:

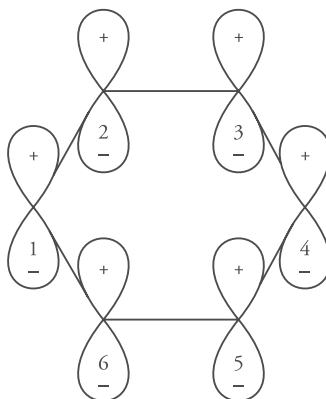


Figure 10.10 *p orbitals of benzene*

The Huckel secular equation is

$$\begin{bmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{bmatrix} = 0 \quad (23)$$

The determinant on expansion gives the following polynomial

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \quad (24)$$

the roots are

$$(x - 2)(x - 1)^2(x + 1)^2(x + 2) = 0$$

$$x = -2; +1(\text{twice}), -1(\text{twice}); +2 \quad (25)$$

The energy levels are

$$x = -2 \quad E_1 = \alpha + 2\beta \quad (\text{BMO}) \quad (26)$$

$$x = -1 \quad E_2 = E_3 = \alpha + \beta \quad (\text{Degenerate pair BMO}) \quad (27)$$

$$x = +1 \quad E_4 = E_5 = \alpha - \beta \quad (\text{Degenerate pair ABMO}) \quad (28)$$

$$x = +2 \quad E_6 = \alpha - 2\beta \quad (\text{ABMO}) \quad (29)$$

The molecular orbital diagram of benzene is shown in Figure 10.11.

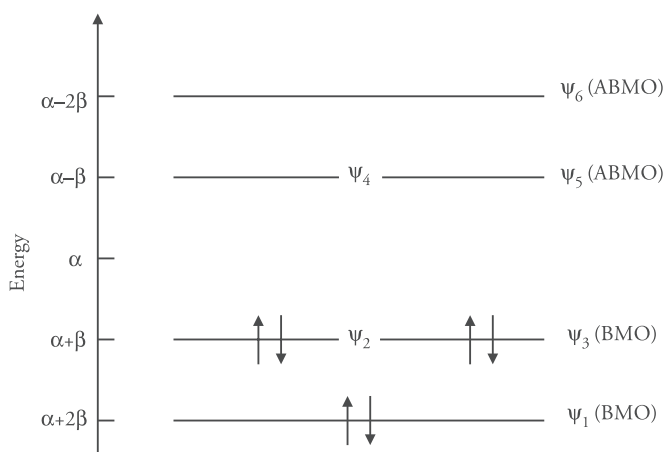


Figure 10.11 HMO diagram for benzene

There are 6π electrons which occupy the orbitals as shown in Figure 10.11.

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

If benzene has three ethene like units in which the double bonds were not interacting with each other its E_π would be $3 \times 2(\alpha + \beta) = 6\alpha + 6\beta$

whereas actually it is $6\alpha + 8\beta$

Hence the resonance or delocalisation energy of benzene is

$$DE = 6\alpha + 8\beta - (6\alpha + 6\beta) = 2\beta$$

$\therefore \beta$ is negative, the energy is lowered by this amount and the molecule is stabilised. The DE of benzene is nearly -460 kJ/mol , hence the molecule is very stable and hence aromatic. The six normalised HMOs are as follows

$$\psi_1 = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\psi_2 = \frac{1}{2}(\phi_1 + \phi_2 - \phi_4 - \phi_5)$$

$$\psi_3 = \frac{1}{\sqrt{12}}(\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6)$$

$$\psi_4 = \frac{1}{2}(\phi_1 - \phi_2 + \phi_4 - \phi_5)$$

$$\psi_5 = -\frac{1}{\sqrt{12}}(\phi_1 + \phi_2 - 2\phi_3 + \phi_4 + \phi_5 - 2\phi_6)$$

$$\psi_6 = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

Huckel $4n+2$ rule of aromaticity :Huckel states that an aromatic compound must contain delocalised π electrons above and below the plane of the molecule. However the delocalisation alone is not enough, the π electron clouds must contain $(4n+2)\pi$ electrons where $n = 0,1,2,3,\dots$. Hence according to Huckel system having 2,6,10,14,18 ... π electrons would be aromatic.

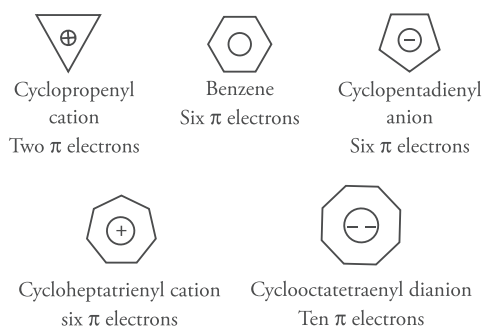


Figure 10.12 Aromatic ions

The bonding and antibonding MOs of a few common aromatic compounds are given in Figure 10.13.

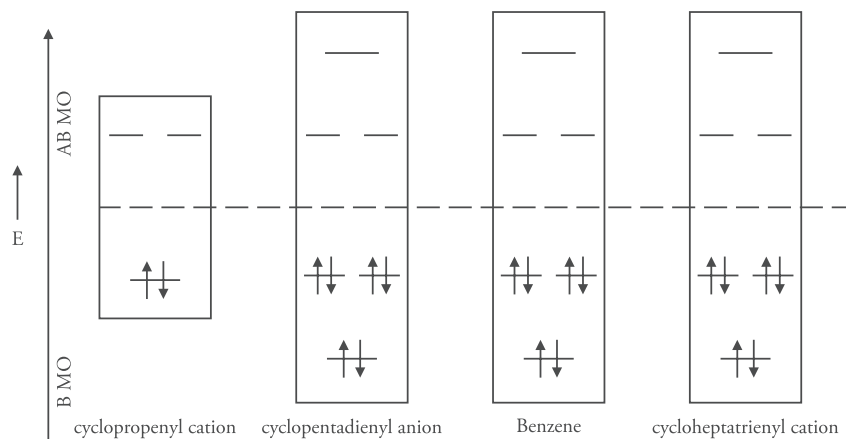


Figure 10.13 MO diagrams of few aromatic compounds

10.10 Chemical Bonding

Matter is made up of atoms. Atoms combine to form molecules, which in turn make up all matter. The atoms in the molecules are held together by attractive forces. These attractive forces, which hold the constituent particles of the molecule together, are known as the chemical bond.

Students at this level are well aware that chemical bonds can be formed by electrostatic attraction between the atoms or ions (ionic bonds) or by the sharing of electrons between the constituent particles (covalent bond). Properties of metals cannot be explained in terms of either ionic or covalent bonds. They are explained by different kinds of bonds called metallic bonds. The molecules acquire different shapes because of bond formation. Different theories have been proposed to explain the distribution of electrons and the shape of the molecules. To describe the bonding in molecules, valence bond theory based on the quantum mechanical model was first proposed by W. Heitler and F. London in 1927 and later developed by Pauling and Slater.

Valence bond theory helps to visualize the sharing of electrons in a covalent bond. The theory says that

- Covalent bond formation takes place when the two combining atoms come closer to each other so that the orbital of one overlaps with that of other.
- The overlapping atomic orbitals must have an unpaired electron with opposite spin.
- Owing to overlapping a new localised bond orbital is formed in which the probability of finding the electron pair is maximum.
- Strength of the bond depends on the extent of orbital overlap. Greater the overlapping stronger is the bond. Except s orbitals, the other orbitals overlap to form bonds with directional character.
- Greater the overlapping lesser is the bond length.

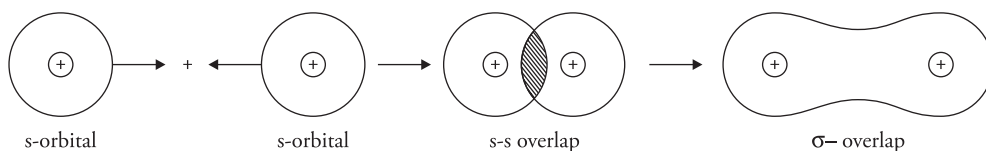
Types of orbital overlapping

On the basis of the type of overlapping, the covalent bonds may be divided into two types

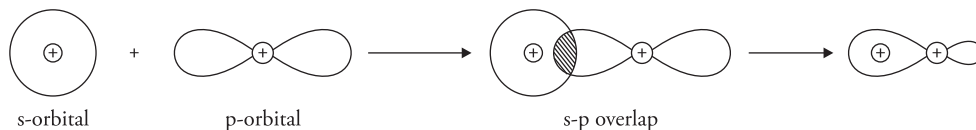
- Sigma (σ) bond and
- pi (π) bond

Sigma (σ) bond A sigma bond is formed between two atoms by the overlap of orbitals along their internuclear axis. The overlap known as axial overlap can be end-to-end or head-to-head overlap. The sigma bond can be formed by three types of combinations of atomic orbital.

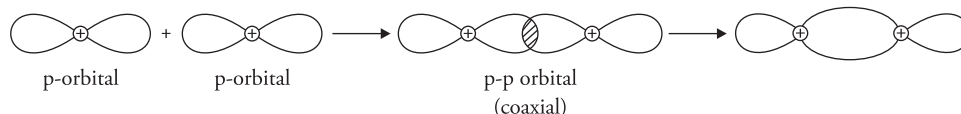
- s-s overlap** In this type, two s orbitals overlap along the internuclear axis forming a covalent bond. For example, two hydrogen atoms overlap to form a sigma bond.



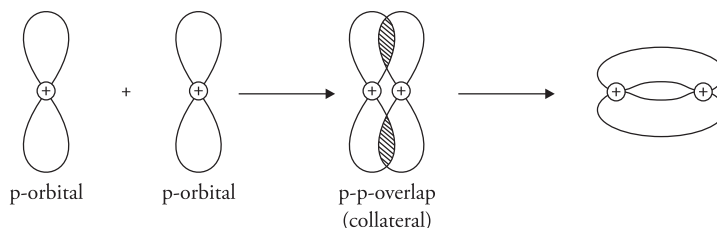
- s-p overlap** When a half-filled s orbital of one atom overlaps with the half filled p orbital of the other atom along the internuclear axis, an s-p overlap resulting in the formation of a sigma bond is said to occur. For example, formation of HCl molecule.



(iii) **p–p overlap (Coaxial)** A sigma bond is formed by p-p overlap when the half filled p orbital from each atom undergoes head on (coaxial overlap) along the internuclear axis.



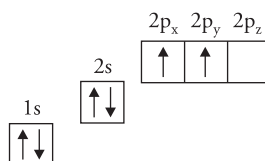
pi (π) bond A π bond is formed by the overlap of two atomic orbitals along the line perpendicular to the molecular axis (sidewise or lateral or collateral overlap). The resulting molecular orbital has two zones of high electron density, one above and the other below the internuclear axis.



A π bond is weaker than a σ bond because of less effective overlap of orbitals in the former. Therefore, the electrons of π bond are mobile.

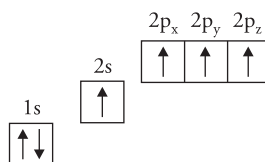
10.11 Hybridisation of Orbitals

The ground-state electronic configuration of carbon is $[\text{He}] 2s^2 2p_x^1 2p_y^1$. It can be represented as



Carbon in the ground state

We can see from the above configuration that carbon has only two unpaired electrons; hence, it should form only two covalent bonds. However, carbon is known to be tetravalent, which can be explained by exciting one of the two 2s electrons to the empty 2p_z orbital as shown below.



Carbon in excited state

The electronic configuration shown above reveals that there are two types of unpaired electrons (one 2s and three 2p) which should form two types of covalent bonds. But it is a known fact that in most of the compounds of carbon like CH_4 , CCl_4 , etc. all the four bonds are equivalent. This was explained by Linus Pauling in 1931 with the help of a new concept known as hybridisation. *In hybridisation, there is intermixing of orbitals of different shapes but almost equal energies. The number of new orbitals formed is equal to the number of intermixing atomic orbitals and the new orbitals are of equivalent energies and shape. The orbitals so formed are called hybrid orbitals.*

Characteristics of Hybridisation

- (i) The number of hybrid orbitals formed is equal to the number of atomic orbitals undergoing hybridisation.
- (ii) Atomic orbitals of the same atom or ion hybridise to form hybrid orbitals of equivalent energy and shape. However they differ from one another with respect to their orientation in space.
- (iii) The bonds formed by hybrid orbitals are more stable than those formed by the pure atomic orbitals.
- (iv) The type of hybridisation helps in predicting the geometry of the molecule.

Types of Hybridisation

1. **sp^3 hybridisation (tetrahedral hybridisation).** When the hybridisation involves one s and three p atomic orbitals it is called as sp^3 (read as sp three and not sp cube) hybridisation. Four sp^3 hybrid orbitals are formed which are arranged tetrahedrally, because in tetrahedral arrangement the four orbitals have a maximum bond angle of 109.5° and thus there is minimum repulsion between the orbitals (Fig. 10.14).

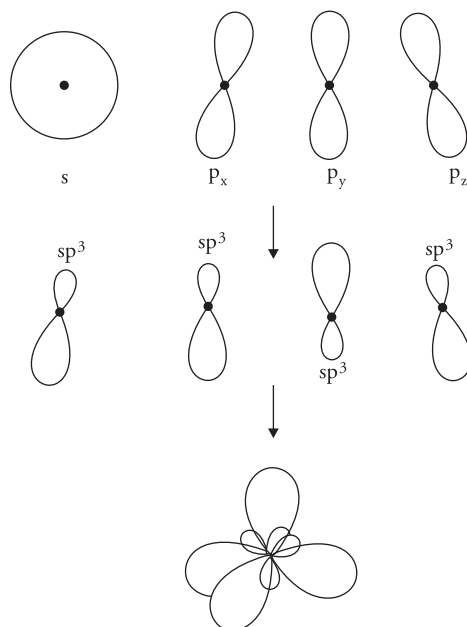


Figure 10.14 Formation of sp^3 hybrids

The Orbital Structure of Methane and Ethane

In methane, the four sp^3 hybrid orbitals of carbon overlap with the four s atomic orbitals of four hydrogen atoms to form four σ bonds as shown in Figure 10.15.

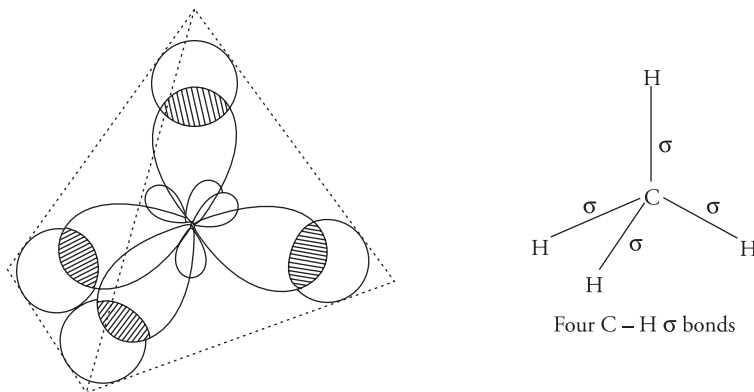


Figure 10.15 *Orbital structure of methane*

In ethane, out of the four sp^3 hybrid orbitals, three hybrid orbitals overlap with the three s atomic orbitals of hydrogen atom and the fourth sp^3 hybrid orbital overlaps with the sp^3 hybrid orbital of the other carbon atom as shown in Figure 10.16.

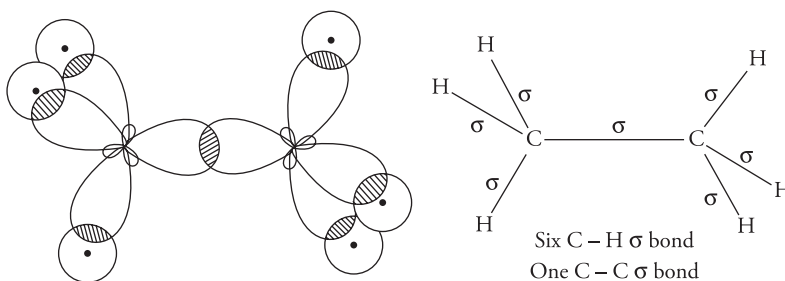


Figure 10.16 *Orbital structure of ethane*

2. **sp^2 hybridisation (trigonal hybridisation)** In sp^2 hybridisation (read as sp two and not sp square) three sp^2 hybrid orbitals are formed by the overlap of one s and $2p$ pure atomic orbitals. sp^2 hybrid orbitals thus formed are coplanar and lie in the same plane at an angle of 120° with each other in a trigonal arrangement as shown in Figure 10.17. The third p orbital does not participate in hybridisation and retains its original dumb-bell shape. It is oriented perpendicular to the plane containing the three sp^2 hybrid orbitals as shown in Figure 10.17.

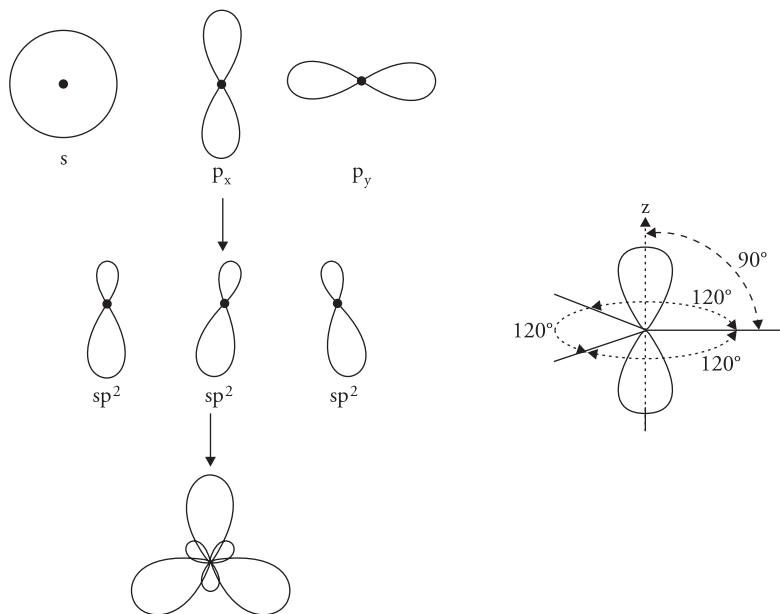
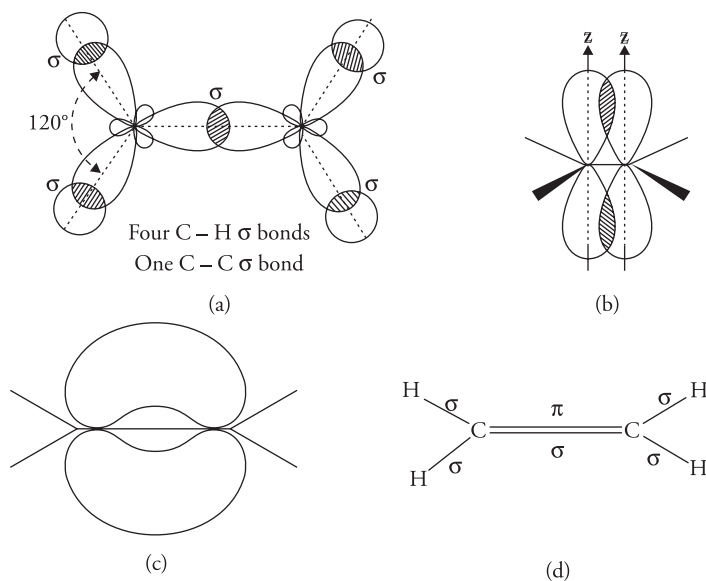


Figure 10.17 (a) Formation of sp^2 hybrid orbitals (b) The unhybridised p orbital

Orbital Structure of Ethene (ethylene)

In ethylene, the two sp^2 hybrid orbitals of each carbon overlap with two s orbitals of two hydrogen atoms; the third sp^2 orbital of one carbon overlaps with that of the other forming five σ bonds in all. The unhybridised p_z orbital of one carbon overlaps sideways (collaterally) with that of the other forming a π bond. The orbital structure of ethene is shown in Figure 10.18.



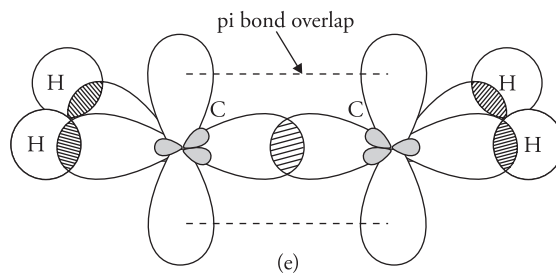


Figure 10.18 (a) The σ bonds in ethene, (b) the p_z orbitals, (c) the σ orbital of ethene, (d) the line formula of ethene showing σ and π bonds, (e) complete structure of ethene

3. **sp hybridisation** A linear combination of one s and one p atomic orbitals gives rise to two sp hybrid orbitals. The two sp hybrid orbitals so formed are at an angle of 180° , that is, they are in a straight line (linear or diagonal arrangement) as shown in (Fig. 10.19a).

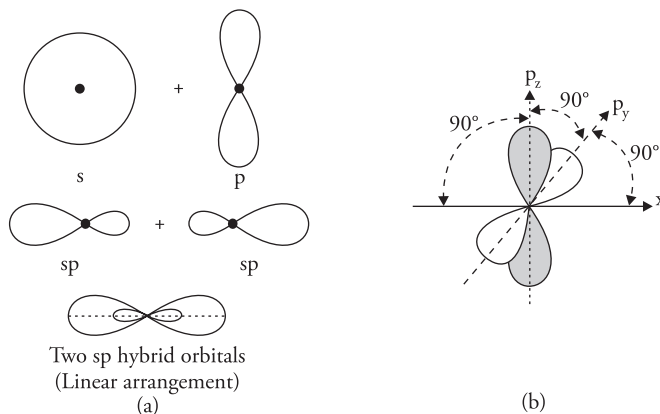
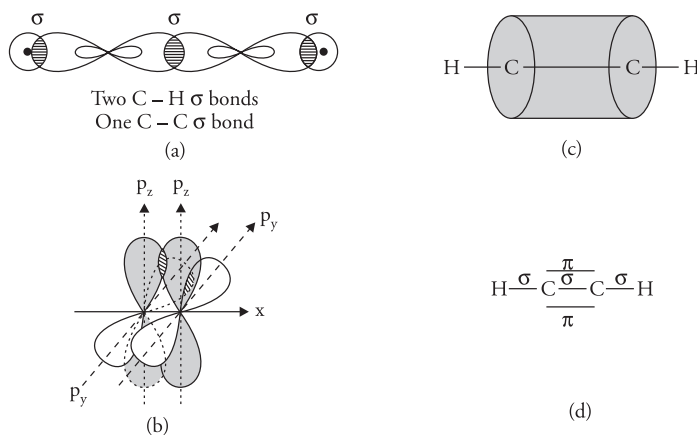


Figure 10.19 (a) Formation of sp hybrids, (b) The unhybridised p orbitals



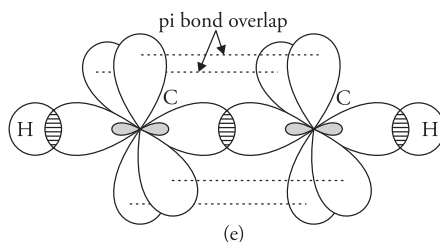


Figure 10.20 (a) The σ bonds in ethyne (b) the p_y and p_z orbitals (c) the cylindrical π cloud of ethyne (d) the line formula of ethyne showing σ and π bonds (e) complete molecular orbital diagram of ethyne

The other two unhybridised p orbitals lie perpendicular to each other and are also perpendicular to the axis containing the two sp hybrid orbitals as shown in Figure 10.20(b).

Orbital Structure of Ethyne (acetylene)

Ethyne molecule has three σ bonds, two of which are formed by the overlap of sp-s orbitals of carbon and the hydrogen atoms, respectively, and the third is formed by the overlap of the sp hybrid orbitals of the two carbon atoms. The unhybridised p orbitals (p_y and p_z) of the two carbon atoms overlap with each other, forming two π bonds as shown in Figure 10.20.

Hybridisation in Boron and Beryllium Compounds

- Shape of BeF_2 molecule** The electronic configuration of beryllium $1s^2 2s^2$. The divalency of Be can be explained by considering the promotion of one of the 2s electrons to the vacant 2p orbital. The 2s and 2p orbitals then get hybridised to form two sp hybrid orbitals that are linearly arranged. Each of these orbitals overlap with 2p orbital of fluorine to form two Be-F bonds. Thus, BeF_2 is linear with a bond angle of 180° . This is shown below

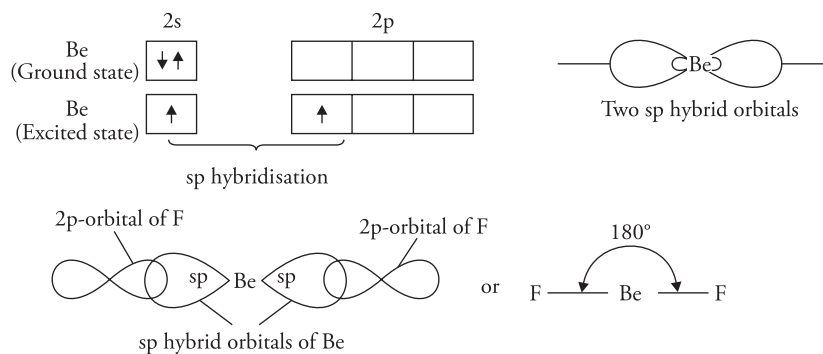


Figure 10.21 sp hybridisation in BeF_2 molecule

- Shape of BF_3 molecule** In BF_3 , the central boron atom has $1s^2 2s^2 2p^1$ electronic configuration. The boron atom is trivalent, which can be explained by considering that one of

the electrons of 2s orbital is promoted to the 2p orbital and these three orbitals (one s and two 2p) then hybridise to form three sp^2 hybrid orbitals having a planar triangular arrangement. Each of these sp^2 hybrid orbitals overlaps with p orbitals from fluorine to form three $B-F$ bonds giving a planar triangular BF_3 molecule with the bond angles of 120° .

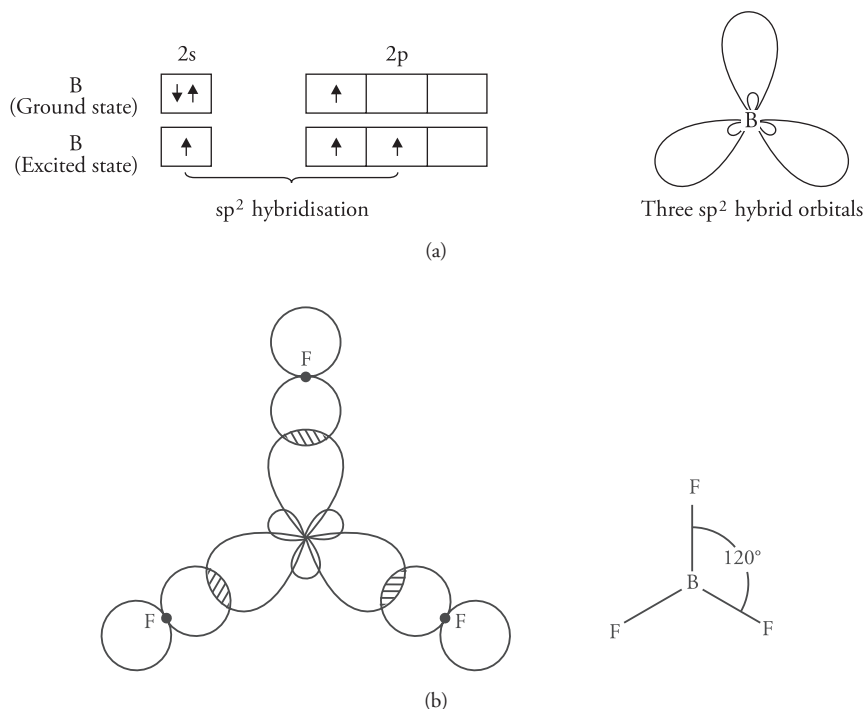


Figure 10.22 (a) sp^2 hybridisation in BF_3 (b) The BF_3 molecule

Hybridisation involving d orbitals

In addition to the s and p orbitals, the elements of the third period contain d orbitals. The energies of 3d orbitals are comparable to the energies of 3s and 3p orbitals; hence, these elements can expand their octets and exhibit covalencies of 5, 6 and even 7. However, in absence of d orbitals the corresponding elements of the second period such as N and O cannot expand their octets. Let us discuss some common types of hybridisation involving d orbitals.

- (a) **sp^3d hybridisation.** In sp^3d hybridisation, five sp^3d hybrid orbitals are formed by the combination of five atomic orbitals (one s, three p and one d) as shown in Figure 10.23. The five hybrid orbitals are arranged such that three of them lie in one plane and make an angle of 120° with one another. They are directed towards the corners of an equilateral triangle and the other two lie perpendicular to the plane assuming a trigonal bipyramidal geometry.

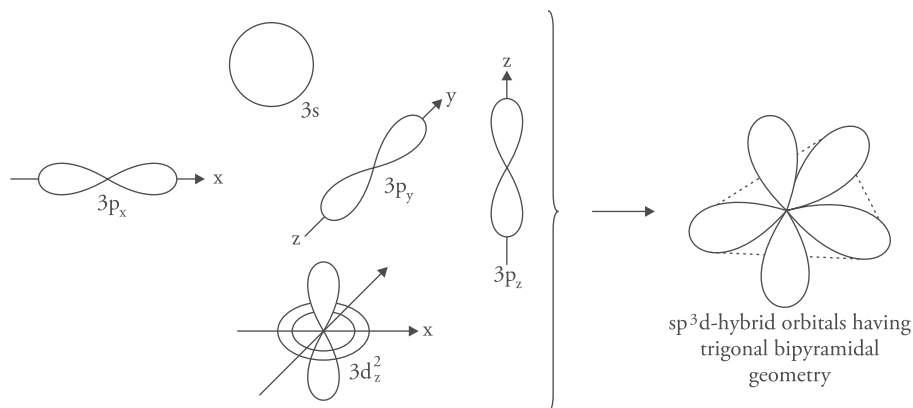


Figure 10.23 Formation of five sp^3d hybrid orbitals that adopt trigonal bipyramidal geometry

Phosphorus pentafluoride involves sp^3d hybridisation as described below

Geometry of PF_5 molecule Phosphorus has an outer electronic configuration of $3s^2 3p^3$, which may be represented as shown in Figure 10.24a. It has three unpaired electrons in the ground state

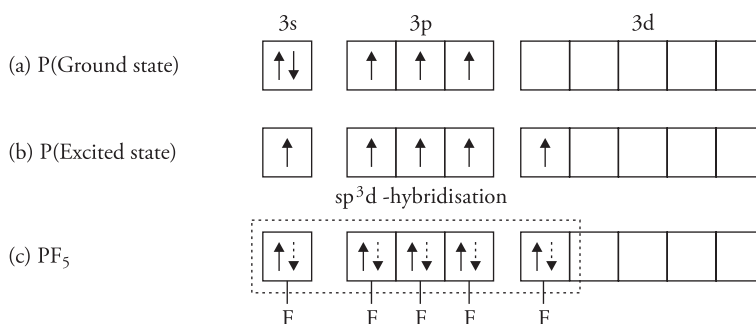


Figure 10.24 Formation of PF_5 molecule involving sp^3d hybridisation

In the excited state, one electron from $3s$ orbitals is promoted to the higher $3d$ orbital, giving rise to five unpaired electrons. (Fig. 10.24). Five sp^3d hybrid orbitals are formed by the mixing of five atomic orbitals (one s + three p + one d orbital), which adopt a trigonal bipyramidal geometry. These sp^3d hybrid orbitals overlap with five $2p$ orbitals of fluorine forming five P–F bonds as shown in Figure 10.25.

Thus, the PF_5 molecule has *trigonal bipyramidal* geometry. Three bonds termed as equatorial bonds lie in one plane at an angle of 120° to one another as in a triangular planar arrangement. The other two bonds termed as axial bonds lie perpendicular to the plane (one above the plane and the other below it) making an angle of 90° with the plane. It may be remembered

that this geometry is not symmetrical as the axial bonds have been found to be larger than the equatorial bonds. In case of PF_5 molecule.

Each P–F axial bond = 158 pm

and each P–F equatorial bond = 153 pm

The larger bond length of axial bond in comparison with equatorial bond is because of greater repulsion from other bonds in axial position.

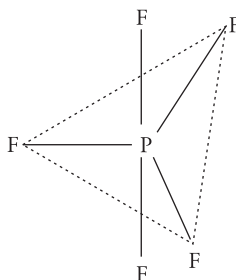


Figure 10.25 Structure of PF_5 molecule

- (b) **sp^3d^2 hybridisation** Combination of one s, three p and two d atomic orbitals gives six equivalent sp^3d^2 hybrid orbitals. These hybrid orbitals adopt an octahedral arrangement and are directed toward the corners of a regular octahedron as given in Figure 10.27.

Geometry of SF_6 molecule The ground-state configuration of sulphur atom (central atom) is $3s^2 3p^4$ (Fig. 10.26). In the excited state, one electron each from 3s and $3p_x$ orbitals is promoted to 3d orbitals as shown in Figure 10.26. These six orbitals get hybridised to form six sp^3d^2 hybrid orbitals. Each of these sp^3d^2 hybrid orbitals overlaps with 2p orbital of fluorine to form a S–F bond. The dotted arrows represent the electrons from F atoms.

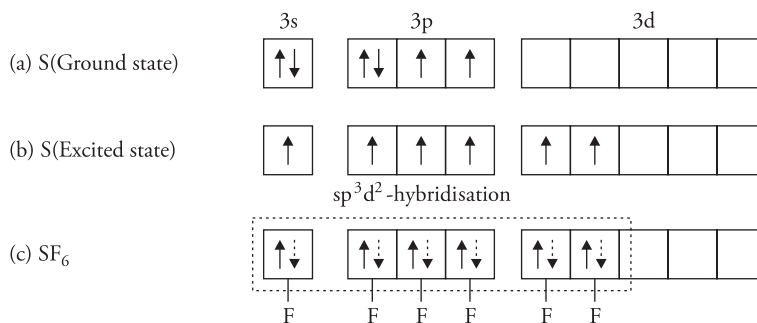


Figure 10.26 Formation of SF_6 molecule involving hybridisation

Thus, SF_6 molecule has octahedral structure as shown in Figure 10.27.

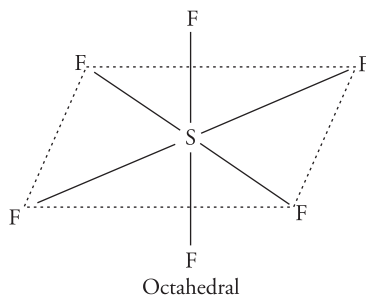


Figure 10.27 Octahedral geometry of SF_6 molecule

- (c) **sp^3d^3 -hybridisation** Seven atomic orbitals one s, three p and three d intermix to form seven sp^3d^3 hybrid orbitals that are directed towards the corners of a pentagonal bipyramid. These hybrid orbitals are not equivalent and five of them are directed toward the vertices of a regular pentagon and two are oriented perpendicular to the plane containing the five hybrid orbitals. IF_7 molecule undergoes sp^3d^3 hybridisation.

Geometry of IF_7 molecule The outer electronic configuration of iodine is $5s^2 5p^5$. In the excited state, electrons from one s and two p orbitals are promoted to vacant 5d orbitals as shown in Figure 10.28. These seven orbitals are then hybridised to give seven sp^3d^3 hybrid orbitals. Each of these sp^3d^3 hybrid orbital overlaps with 2p orbitals of fluorine to form IF_7 molecule having pentagonal bipyramidal geometry.

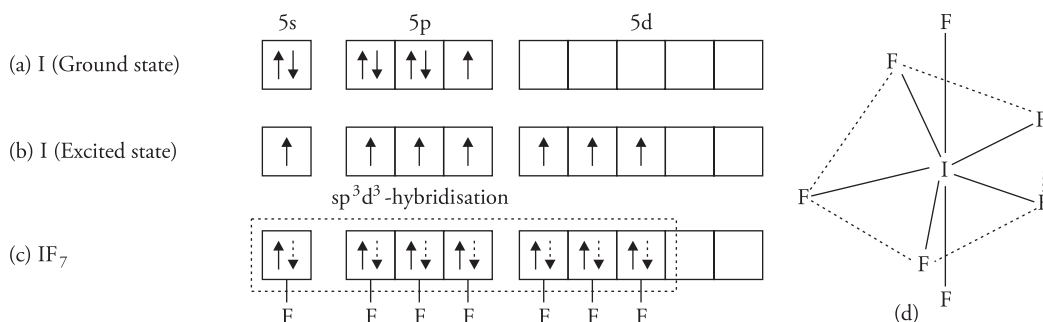


Figure 10.28 (a-c) Formation of IF_7 molecule involving sp^3d^3 hybridisation, (d) pentagonal bipyramidal geometry of IF_7 molecule

In this geometry, all the bond angles are not equal. Five F atoms are directed towards the vertices of a pentagon making an angle of 72° . The other two F atoms are at right angle (90°) to the plane. These bonds are of different lengths. The axial bonds are larger than the equatorial bonds.

- (d) **dsp^2 hybridisation** Compounds of transition metal ions generally show dsp^2 hybridisation. Four atomic orbitals one d ($d_{x^2-y^2}$), one s and two p intermix to form four dsp^2 hybrid orbitals that adopt square planar geometry.

Geometry $[\text{Ni}(\text{CN})_4]^{2-}$ The complex ion $[\text{Ni}(\text{CN})_4]^{2-}$ involves dsp^2 hybridisation as explained below. In this case, the oxidation state of nickel is + 2. The outer electronic configuration of Ni^{2+} is 3d^8 as given in Figure 10.29. During complex formation, the two unpaired electrons are paired up making one 3d orbital empty.

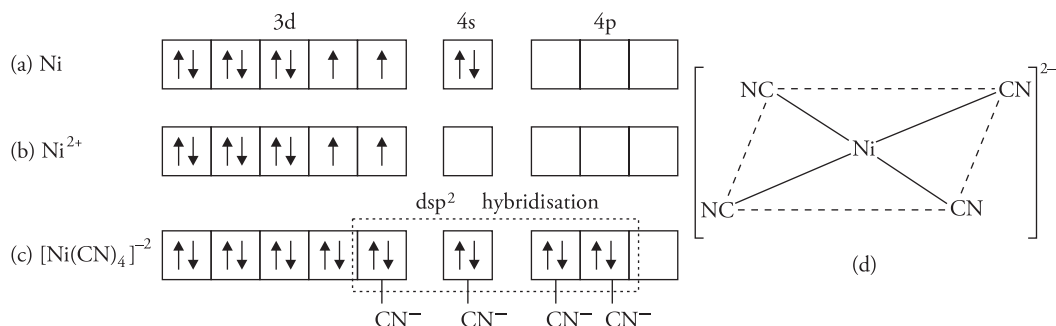


Figure 10.29 (a-c) Formation of $[\text{Ni}(\text{CN})_4]^{2-}$ involving dsp^2 hybridisation, (d) structure of $[\text{Ni}(\text{CN})_4]^{2-}$

Four empty orbitals (3d, 4s and two 4p) hybridise to form four dsp^2 hybrid orbitals that acquire a square planar arrangement. Each one of the four CN groups donates lone pair of electrons to vacant hybrid orbitals forming four Ni–CN bonds. The ion $[\text{Ni}(\text{CN})_4]^{2-}$ has square arrangement as shown in Figure 10.29.

Hybridisation in NH_3 molecule

In NH_3 molecule, nitrogen is the central atom whose valence shell configuration is $1\text{s}^2, 2\text{s}^2, 2\text{p}_x^1, 2\text{p}_y^1, 2\text{p}_z^1$

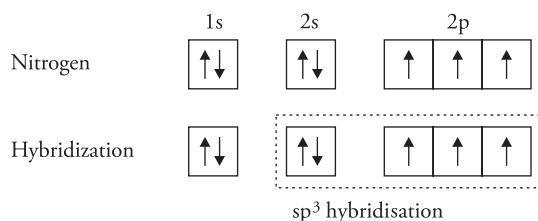


Figure 10.30 Hybridisation in NH_3

One s (completely filled) and three p (half filled) orbitals hybridise together to form four sp^3 hybrid orbitals. Three hybrid orbitals are singly occupied and form bond with the hydrogen atom. The fourth orbital having a lone pair of electrons does not take part in bond formation. As the molecule is sp^3 hybridised, it should have a tetrahedral geometry but it is found to be pyramidal in shape. This is because the lone pair of electrons repels the bond pair; hence, NH_3 has a distorted tetrahedral or pyramidal shape and the bond angle reduces from $109^\circ 28'$ to $107^\circ 48'$.

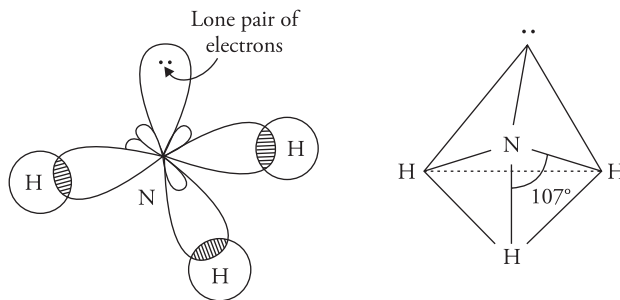


Figure 10.31 *Pyramidal structure of NH_3*

Hybridisation in H_2O molecule

The valence shell configuration of the central oxygen atom is $1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

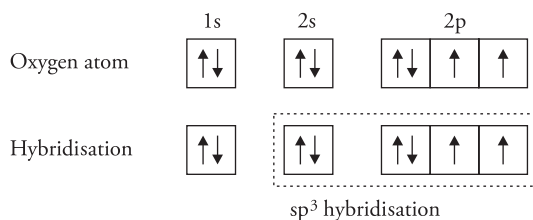


Figure 10.32 *Hybridisation in H_2O*

One s orbital (completely filled) and three p orbitals (one completely filled and two half filled) hybridise to form four sp^3 hybrid orbitals. Two singly occupied hybrid orbitals are utilized for bond formation with the two hydrogen atoms and the two hybrid orbitals containing the lone pairs of electrons do not take part in bond formation. The structure should be tetrahedral (sp^3 hybridisation) but the presence of two lone pairs distorts the geometry of the molecule and it becomes V-shaped reducing the bond angle from $109^\circ 28'$ to $104^\circ 27'$.

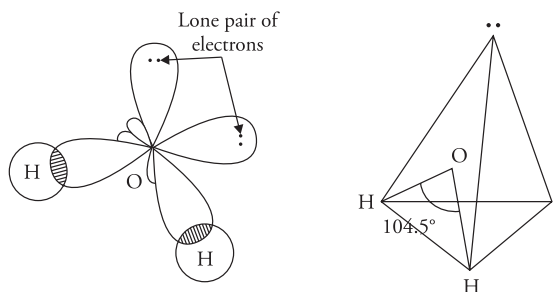


Figure 10.33 *Shape of water molecule*

Hybridisation in SF_4 molecule The valence shell configuration of the central sulphur atom is $3s^2, 3p_x^2, 3p_y^1, 3p_z^1$.

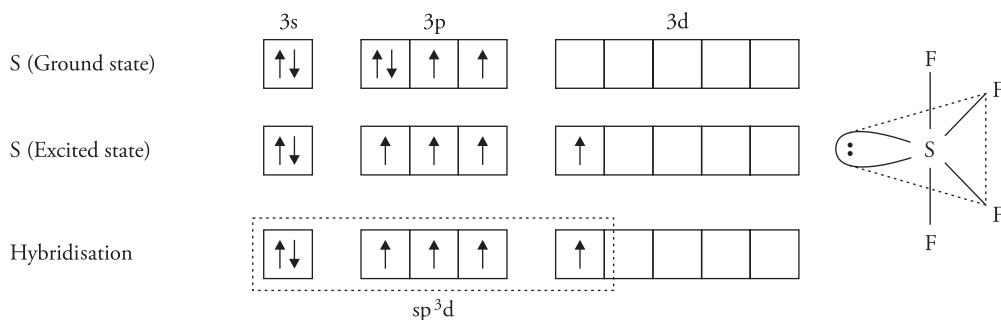


Figure 10.34 Hybridisation in SF_4 molecule

An electron from the $3p$ orbital is promoted to empty $3d$ orbital, thus making available four unpaired orbitals. These five atomic orbitals one s , $3p$ and one d hybridise to form five sp^3d hybrid orbitals. Out of these five, one accommodates the lone pair and the other four form bonds with fluorine atoms. The shape of the molecule is trigonal bipyramidal. The expected bond angles are 90° , 120° and 180° . However, the presence of lone pair in one of the hybridised orbital reduces the bond angle to 89° , 118° and 177° instead of 90° , 120° and 180° , respectively. The lone pair occupies equatorial position.

Hybridisation in SnCl_2 molecule The valence shell configuration of the central tin atom is $5s^2, 5p_x^1, 5p_y^1$.

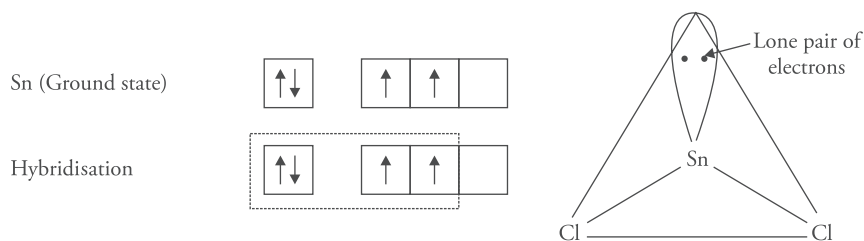


Figure 10.35 Hybridisation in SnCl_2 molecule

sp^2 hybridisation takes place giving rise to three hybrid orbitals. One accommodates the lone pair and the other two half-filled orbitals form bonds with chlorine atoms. The shape of the molecule should be trigonal planar (sp^2 hybridisation) with the bond angle of 120° ; however, the presence of lone pair of electrons causes repulsion and the bond angle reduces and SnCl_2 acquires a V-shaped geometry (Fig. 10.35).

10.12 Molecular Orbital Theory

In 1932, Hund and Mulliken had put forward the molecular orbital theory. The main features of this theory are as follows

- (i) New orbitals termed as the molecular orbitals are formed by the overlap of atomic orbitals of the combining atoms. The atomic orbitals lose their individual identity after the formation of the molecular orbitals.
- (ii) The number of molecular orbitals formed is equal to the number of atomic orbitals involved in their formation.
- (iii) The electron in an atomic orbital is influenced by just one positive nucleus of the atom, that is, it is monocentric, whereas depending upon the number of atoms in the molecule the electron of a molecular orbital is under the influence of more than one nuclei, that is, it is polycentric.
- (iv) Similar to the atomic orbitals, the filling of electrons in the molecular orbitals also follows the Aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle.
- (v) Atomic orbitals with comparable energies as well as proper orientations combine to form molecular orbitals.

Linear Combination of Atomic Orbitals (LCAO)

According to wave mechanics, the atomic orbitals can be expressed by wave function (ψ), which represent the amplitude of the electron waves. The values of these wave functions can be obtained by the solutions of Schrodinger wave equation. Just like atoms, the Schrodinger wave equation can also be applied to molecules. The wave function for molecular orbitals is obtained by the linear combination of atomic orbitals (LCAO).

To explain the LCAO concept, let us consider two atoms A and B having the wave functions ψ_A and ψ_B . According to the LCAO concept, molecular orbitals are formed by the linear combination of atomic orbitals. The combination can take place by addition (constructive interaction) or subtraction (destructive interaction) of the wave functions of atomic orbitals. These two types of combinations give rise to two molecular orbitals as described below.

- (i) Bonding molecular orbitals are obtained by the addition of wave functions of atoms and may be represented as

$$\psi(\text{MO}) = \psi_A + \psi_B \quad (\text{Constructive interaction}).$$

The bonding MO has energy lower than the energy of the atomic orbitals from which it is formed and this difference of energy is termed as the stabilisation energy.

- (ii) Antibonding molecular orbitals are obtained by the subtraction of wave function of atoms and may be represented as

$$\psi^*(\text{MO}) = \psi_A - \psi_B \quad (\text{Destructive interaction}).$$

An asterisk * represents the antibonding molecular orbital. The antibonding molecular orbital has energy higher than that of the constituent overlapping atomic orbitals. The difference in energy between the antibonding molecular orbital and the combining atomic orbitals is called

the destabilisation energy. Thus, antibonding MO destabilises the molecule. *It is important to note that the bonding MO is stabilised to the same extent as the antibonding MO is destabilised* (Fig. 10.36).

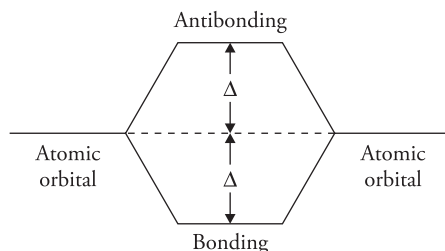


Figure 10.36 Formation of bonding and antibonding molecular orbitals

Moreover, when bonding MO is formed the two waves are in phase and the amplitude gets added up. Therefore, the resulting wave function has more electron density in between the nuclei. On the other hand, in the formation of antibonding MO the two waves are out of phase, there is destructive interference and the amplitudes of the waves get subtracted or cancelled. This gives rise to nodal plane between the two nuclei.

Probability Density in Bonding and Antibonding MOs

The probability density in bonding and antibonding molecular orbitals is given by the square of wave function (ψ^2).

For Bonding MO

$\psi = \psi_A + \psi_B$, so that

$$\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B$$

Thus, ψ^2 is greater than $\psi_A^2 + \psi_B^2$ (sum of the probability densities of individual atoms) by an amount equal to $2\psi_A \psi_B$. Therefore, the probability of finding electrons in bonding MO is greater than in either of the atomic orbitals (ψ_A or ψ_B).

For Antibonding MO

$\psi^* = \psi_A - \psi_B$, so that

$$\psi^{*2} = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A \psi_B$$

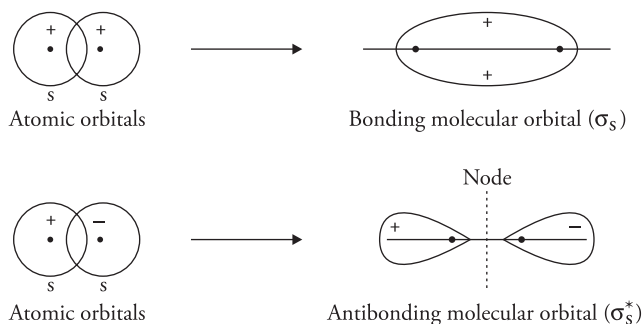
Thus, ψ^{*2} is less than $\psi_A^2 + \psi_B^2$ by an amount equal to $2\psi_A \psi_B$. Therefore, the probability of finding the electrons in antibonding MO is less than in either of the atomic orbitals (ψ_A or ψ_B).

Molecular orbitals from 1s, 2s and 2p atomic orbitals

When two atomic orbitals overlap, along the internuclear axis, then the resulting molecular orbitals are the sigma (σ) molecular orbital. On the other hand, if the atomic orbitals overlap sideways then the pi (π) molecular orbital is formed.

Combination of s-s atomic orbitals

1s with 1s or 2s with 2s



[Note that + and – are signs of wave function and have nothing to do with electrical charges.]

Figure 10.37 s-s overlap of orbitals

Combination of s-p atomic orbitals

Combination of s orbital with p orbital occurs provided the lobes of p are directed along the internuclear axis. Bonding MOs are formed when lobes of the same sign overlap and antibonding MO are formed when lobes of opposite signs overlap.

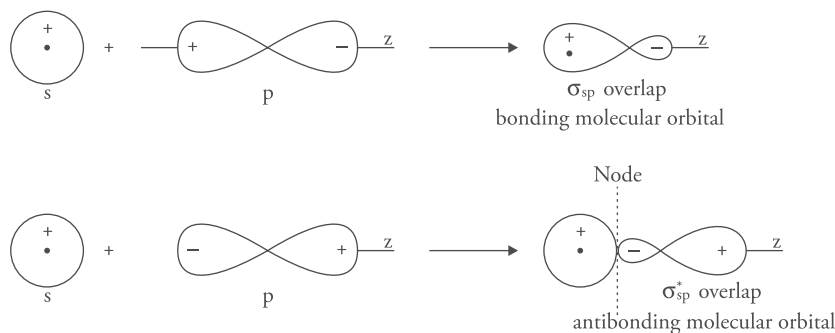


Figure 10.38 s-p overlap of orbitals

Combination of p-p atomic orbitals

There are three types of p orbitals directed along the cartesian coordinates x , y , and z , respectively. By convention the z -axis is assumed as the internuclear axis. The $2p_z$ atomic orbitals overlap along the internuclear axis forming σ and σ^* molecular orbitals whereas $2p_x$ and $2p_y$ orbitals overlap collaterally forming π and π^* molecular orbitals.

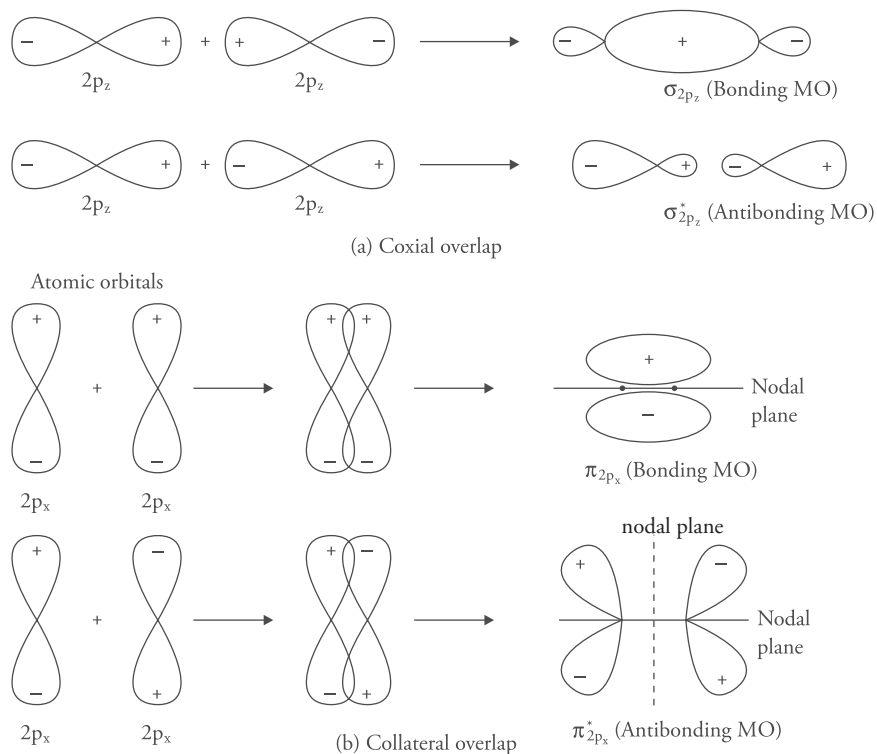


Figure 10.39 *p-p overlap of orbitals: (a) coaxial overlap; (b) collateral overlap*

Combination of p-d orbitals

Bonding and antibonding orbitals may also be formed by the overlap of p orbital of one atom with d orbital of the other atom. As the overlapping is lateral, the molecular orbitals are designated as π orbitals.

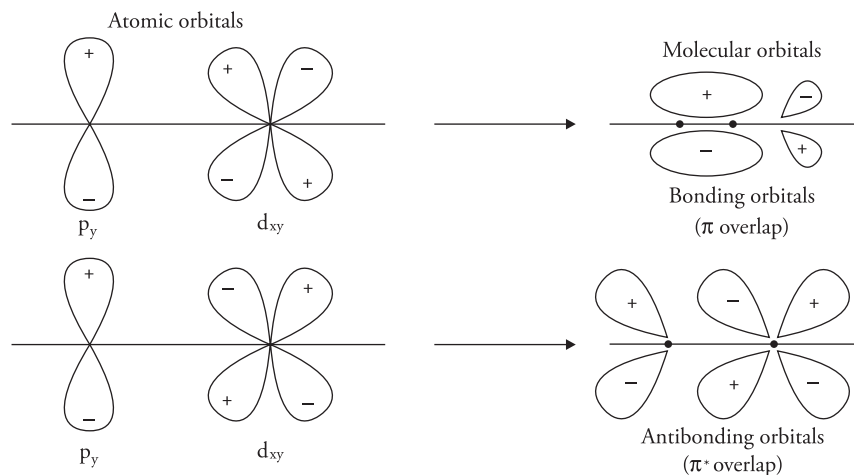


Figure 10.40 *p-d overlap of orbitals*

Combination of d-d orbitals

Bonding and antibonding orbitals formed by the overlap of two d orbitals are termed as δ and δ^* , respectively.

Conditions for the effective overlap of Atomic Orbitals

For effective combination,

- The energies of combining atomic orbitals should be nearly same/comparable.
- The extent of overlapping should be large.
- The symmetry of the combining atomic orbitals around the internuclear axis should be the same. For example, $2s$ atomic orbital of one atom combines with $2s$ or $2p_z$ orbital of the other atom but not with the $2p_y$ or $2p_x$ orbitals, because when $2s$ of one atom overlaps with $2p_x$ or $2p_y$ orbital, a collateral overlap occurs and the $++$ overlap is cancelled by the $+ -$ overlap. Consequently, molecular orbital will not be formed and this situation is termed as non-bonding.

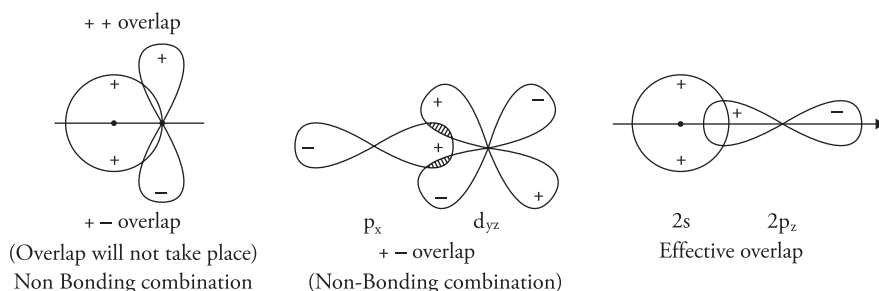
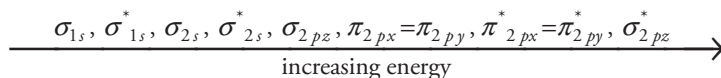


Figure 10.41 Effective and ineffective overlap of orbitals

Energy level Diagram for Molecular Orbitals

Spectroscopic methods are used for the experimental determination of the energy of molecular orbitals. The molecular orbitals obtained by the combination of $1s$, $2s$ and $2p$ atomic orbitals can be arranged in the increasing order of energy as follows



The energy of bonding π_{2px} and π_{2py} molecular orbitals is exactly similar and they are said to be doubly degenerate. Similarly, π_{2px}^* and π_{2py}^* molecular orbitals also have the same energy and are doubly degenerate.

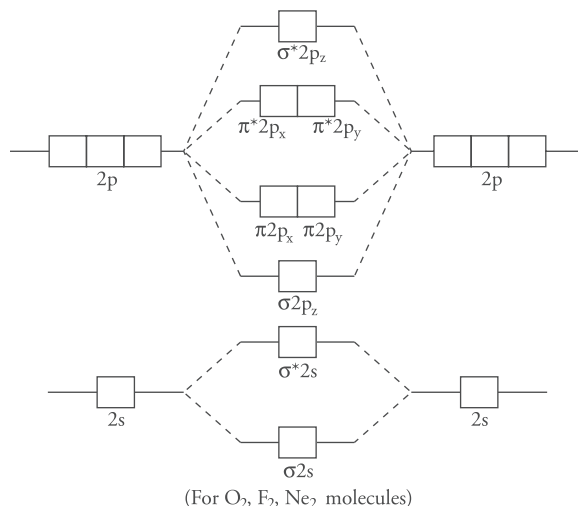
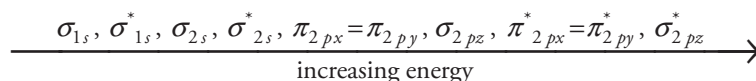


Figure 10.42 Molecular orbital energy level diagram of O_2 , F_2 and Ne_2 molecules

The molecular orbitals of O_2 , F_2 and Ne_2 follow the above-mentioned energy order.

However, as revealed by spectroscopic studies all the molecules do not follow the above-mentioned sequence of energy levels. In Li_2 , Be_2 , B_2 , C_2 and N_2 , the energy of the σ_{2pz} molecular orbital is higher than the energy of π_{2px} and π_{2py} molecular orbitals. The molecular orbitals for these homonuclear diatomic molecules have the following order of energy



The energy level diagram for these molecules is given in Figure 10.43.

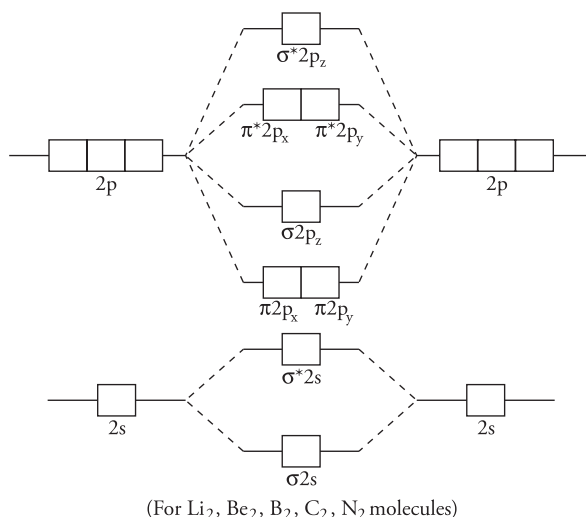


Figure 10.43 Molecular orbital energy level diagram for Li_2 , Be_2 , B_2 , C_2 and N_2

Filling of Electrons in Molecular orbitals

The electrons are filled in the molecular orbitals according to the following rules

1. **Aufbau Principle** The electrons enter the molecular orbitals in the order of their increasing energies. Molecular orbitals of lower energy are filled first.
2. **Pauli's Exclusion Principle** This law states that the maximum number of electrons in any molecular orbital is two and the electrons occupying the same orbital must have opposite spins.
3. **Hund's rule** It states that if two molecular orbitals are of the same energy, then one electron goes to each orbital and electron pairing will start only after all the orbitals of equal energy are singly occupied.

Electronic Configuration and Molecular Behavior

The stability of the molecule, its magnetic behavior and strength can be known with the help of molecular orbital diagram.

- (i) **Stability of the molecule** Bond formation will occur and the molecule will be stable if the total number of electrons in the bonding molecular orbitals is greater than the number of electrons in the antibonding molecular orbitals. On the other hand, the molecule will be unstable if the number of electrons in the antibonding orbitals is more than the number of electrons in the bonding molecular orbitals.
- (ii) **Bond order** It is the number of covalent bonds in the molecule and is equal to half the difference between the number of electrons in the bonding molecular orbitals and the number of electrons in the antibonding molecular orbitals. The stability of a molecule is determined by its bond order.

$$\text{Bond order} = \frac{\text{Number of electrons in bonding MOs} - \text{Number of electrons in antibonding MOs}}{2}$$

Single, double and triple bonds have the bond order of one, two and three, respectively. In some cases, bond order may be fractional.

Bond order conveys the following information

- (a) A negative or zero bond order corresponds to an unstable molecule, whereas positive bond order indicates a stable molecule.
- (b) Bond dissociation energy is directly proportional to the bond order. Higher bond dissociation energy means a stable molecule. For example, nitrogen and oxygen molecules with the bond orders of 3 and 2, respectively, have the bond dissociation energies of 945 and 495 kJ mol⁻¹, respectively.
- (c) Bond order is inversely proportional to bond length. For example,

Molecule	Bond order	Bond length
O ₂	2	121 pm
N ₂	3	110 pm

- (iii) **Magnetic Character** A molecule is diamagnetic if all the electrons are paired and paramagnetic if it has unpaired electrons.

Bonding in Some Homonuclear Diatomic Molecules

Let us discuss bonding in some homonuclear diatomic molecules of the elements of first and second rows of the periodic table.

1. **Hydrogen molecule (H_2)** Hydrogen molecule is formed by the combination of $1s^1$ atomic orbitals of two hydrogen atoms. The hydrogen molecule thus formed has two electrons that are accommodated in the bonding molecular orbital and the antibonding molecular orbital remains vacant. The molecular orbital energy level diagram for H_2 molecule is shown in Figure 10.44.

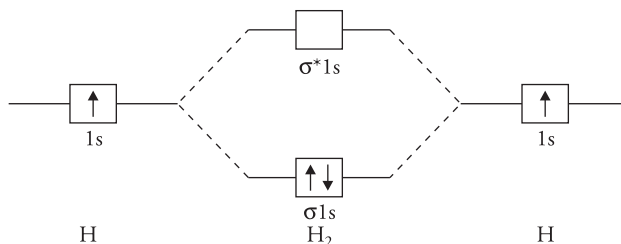
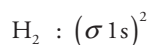


Figure 10.44 Molecular orbital energy level diagram for H_2 molecule

The electronic configuration of H_2 molecule is represented as follows



The bond order in H_2 is

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

Bond order one means that there is a single covalent bond between the two hydrogen atoms. The bond length is found to be 74 pm and the bond dissociation energy is 485 kJ mol^{-1} . Absence of unpaired electron makes the molecule diamagnetic.

2. **Hydrogen molecule ion (H_2^+)** Hydrogen molecule ion is formed by the combination of a hydrogen atom with one electron and a hydrogen ion without an electron. The molecular orbital of H_2^+ ion contains one electron that occupies the bonding molecular orbital. Presence of an unpaired electron makes the molecule paramagnetic. The molecular orbital diagram is given in Figure 10.45.

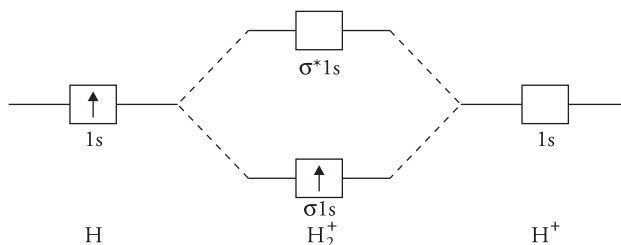


Figure 10.45 Molecular orbital energy level diagram for H_2^+ ion

The electronic configuration of the molecule is $\text{H}_2^+ : (\sigma 1s)^1$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{1 - 0}{2} = \frac{1}{2}$$

As the bond order has a positive value, the molecule is stable. The bond length of H_2^+ ion is larger than that of H_2 molecule (bond length $\text{H}_2^+ = 104$ pm, $\text{H}_2 = 74$ pm), whereas its bond dissociation energy is less than that of H_2 molecule (bond dissociation energy $\text{H}_2^+ = 269$ kJ mol⁻¹, $\text{H}_2 = 485$ kJ mol⁻¹). This clearly supports the fact that bond in H_2^+ ion is weaker than that in H_2 molecule.

3. Hydrogen molecule negative ion H_2^-

A hydrogen atom with one electron in its valence shell and a hydrogen ion with two electrons combine to form H_2^- ion. Thus, H_2^- ion has three electrons and its electronic configuration will be $(\sigma 1s)^2 (\sigma^* 1s)^1$ and

$$\text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

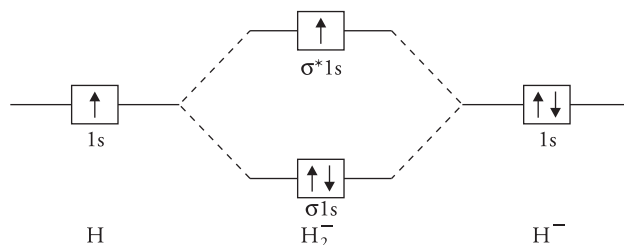
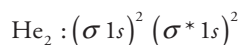


Figure 10.46 Molecular orbital energy level diagram for H_2^- ion

4. **Hypothetical helium molecule (He_2)** Helium atom has the electronic configuration $1s^2$; therefore, He_2 molecule has four electrons in it. These electrons occupy $\sigma 1s$ and $\sigma^* 1s$ MOs as shown in Figure 10.47. The electronic configuration for helium molecule may be written as



$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0$$

The **bond order is zero** that indicates that there is no net bonding and He_2 molecule will not be formed and the same has been proved experimentally.

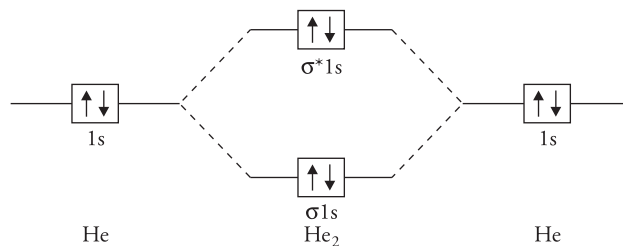
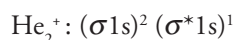


Figure 10.47 Molecular orbital energy level diagram for He₂ molecule (hypothetical)

5. **Helium molecule ion (He₂⁺)** This molecule is formed by the combination of a helium atom containing two electrons and He⁺ ion with one electron. The He₂⁺ ion thus has three electrons that occupy the (σ1s)² and (σ*1s)¹ orbitals. The molecular orbital electronic configuration of the molecule is



$$\text{Bond order} = \frac{2-1}{2} = \frac{1}{2}$$

Positive value of bond order indicates that He₂⁺ is stable and its bond dissociation energy is found to be 242 kJ mol⁻¹. The presence of an unpaired electron makes the molecule paramagnetic.

Lithium molecule The valence shell configuration of lithium atom is 1s²2s¹. Thus, lithium molecule Li₂ has six electrons. These are arranged as (σ1s)² (σ*1s)² (σ2s)². The inner shells do not contribute to bonding; hence, the electronic configuration can be written as KK σ2s² where KK denotes that K shell of the two atoms is complete and does not contribute to bonding.

$$\text{Bond order} = \frac{1}{2}(4-2) = 1$$

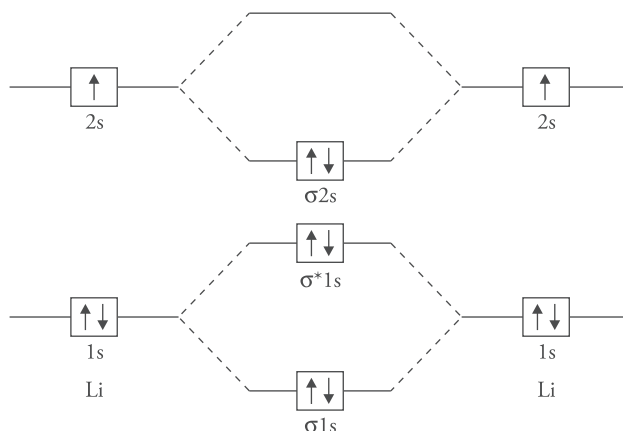


Figure 10.48 Energy level diagram of Li₂

Beryllium molecule Its electronic configuration is $1s^2 2s^2$. Be_2 has eight electrons; hence, its molecular orbital configuration will be $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2$ or it can be written as $\text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2$

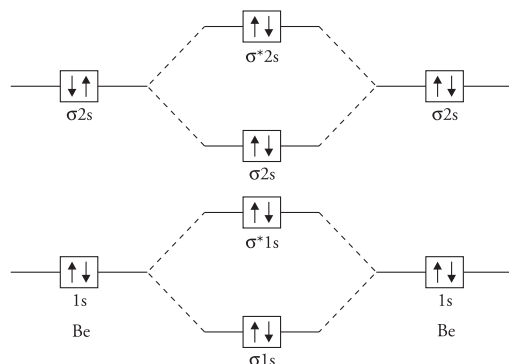


Figure 10.49 Molecular orbital energy level diagram for Be_2

$$\text{Bond order} = \frac{4 - 4}{2} = 0$$

Bond order is zero, hence Be_2 molecule is not formed.

Boron molecule (B_2) The electronic configuration of boron is $1s^2 2s^2 2p^1$. B_2 has 10 electrons. Its molecular orbital configuration will be $\text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1$.

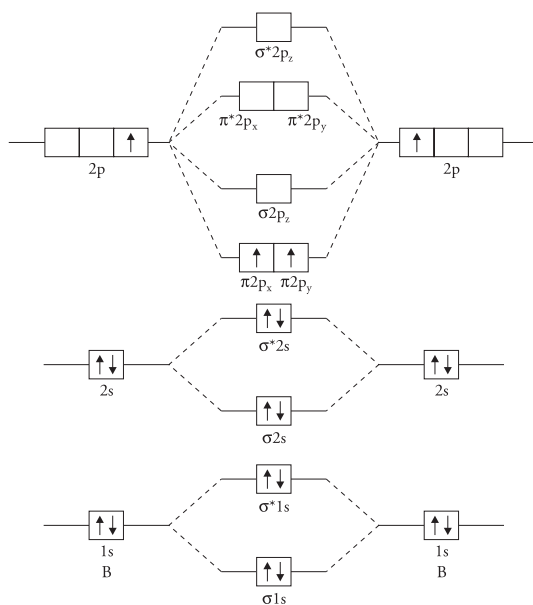


Figure 10.50 Molecular orbital energy level diagram for B_2

$$\text{Bond order} = \frac{1}{2}(6 - 4) = 1$$

As there are two unpaired electrons the molecule is paramagnetic.

Carbon molecule (C_2) A carbon atom has six electrons and its electronic configuration is $1s^2 2s^2 2p^2$. C_2 molecule will have 12 electrons. Its electronic configuration will be $KK (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$.

$$\text{Bond order} = \frac{1}{2}(8 - 4) = 2$$

Although it appears that C_2 is stable, carbon exists as macromolecule in graphite and diamond. In diamond and graphite, each carbon forms four bonds in preference to C_2 .

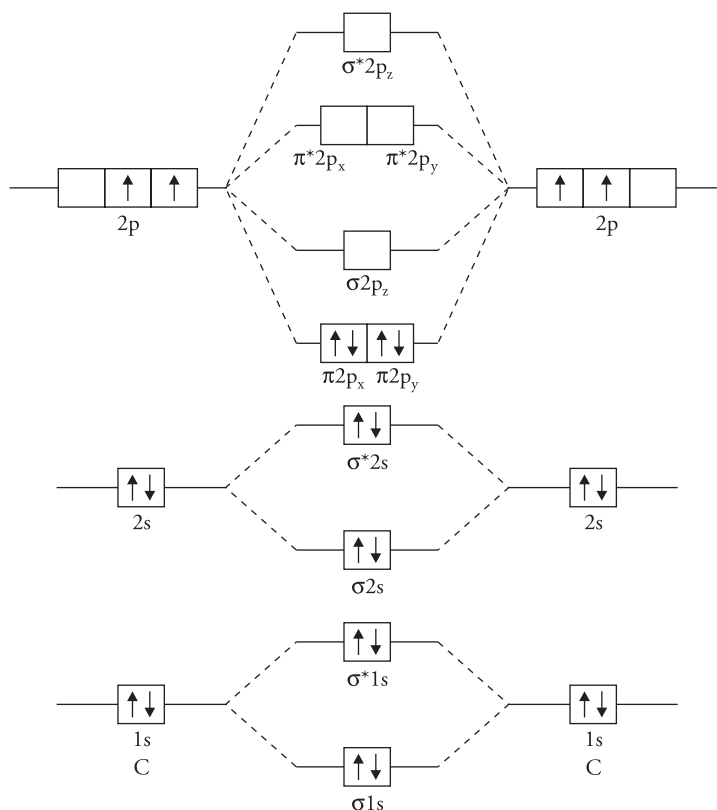


Figure 10.51 Molecular orbital energy level diagram for C_2

Table 10.2 summarises the molecular orbital configuration, bond order and magnetic character of Li_2 , Be_2 , B_2 and C_2 .

Table 10.2 Molecular orbital configurations of Li_2 , Be_2 , B_2 and C_2

Molecule	MO configuration	Bond order	Magnetic character
Li_2	$\text{KK } (\sigma 2s)^2$	1	Diamagnetic
Be_2	$\text{KK } (\sigma 2s)^2 (\sigma^* 2s)^2$	0	Molecule does not exist
B_2	$\text{KK } (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)' = (\pi 2p_y)'$	1	Paramagnetic
C_2	$\text{KK } (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$	2	Diamagnetic

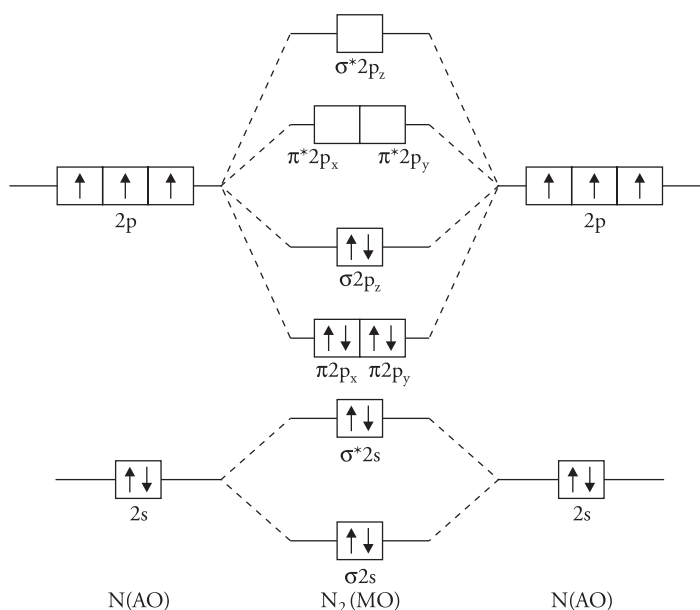
6. **Nitrogen molecule (N_2)** Each of the two nitrogen atoms with an electronic configuration of $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ contributes five valence electrons to the N_2 molecule. The MO diagram is shown in Figure 10.52.

The molecular orbital configuration of the molecule is

$$\text{N}_2 : \text{KK } (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^2$$

$$\text{Bond order} = \frac{8-2}{2} = 3$$

Thus, there are three bonds in the nitrogen molecule, one σ and two π bonds. This is in accordance with very high bond dissociation energy of 945 kJ mol^{-1} and small bond length of 110 pm. The molecule is diamagnetic because it has no unpaired electrons.

**Figure 10.52** Molecular orbital energy level diagram for N_2 molecule

N₂⁺ molecule and its comparison with N₂

N₂ molecule loses one electron to form the N₂⁺ ion. This electron is lost from $\sigma 2p_z$ MO and hence the electronic configuration of N₂⁺ ion will be

$$\text{N}_2^+ : \text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\sigma 2p_z)^1$$

$$\text{Bond order} = \frac{7-2}{2} = 2\frac{1}{2}$$

Bond order of N₂⁺ ion is $2\frac{1}{2}$ and the bond order of N₂ molecule is 3; hence, the N₂⁺ bond is longer and weaker than that of N₂ molecule.

7. Oxygen molecule (O₂)

Oxygen atom with the electronic configuration of $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ has six electrons in its valence shell. The molecular orbitals formed by the overlap of inner 1s atomic orbitals are denoted by KK and it signifies $(\sigma 1s)^2 (\sigma^* 1s)^2$. The remaining 12 electrons are filled in molecular orbitals as shown in Figure 10.53.

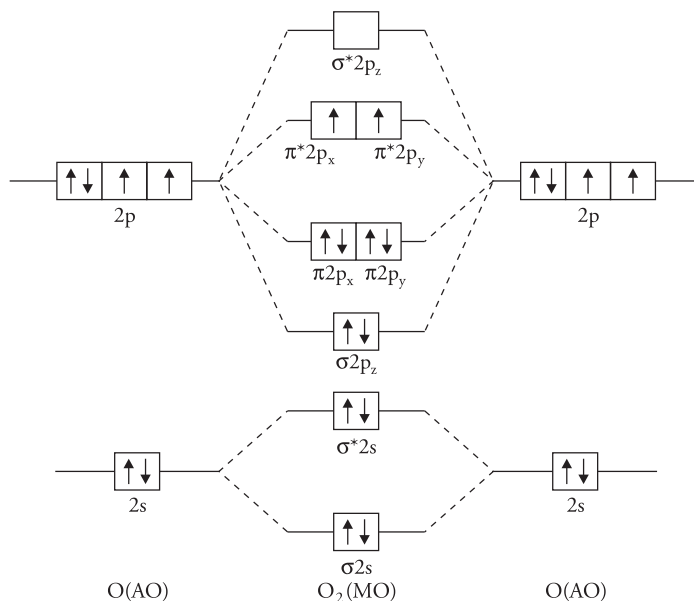


Figure 10.53 Molecular orbital energy level diagram for O₂ molecule

The electronic configuration of the molecule is

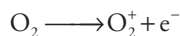
$$\text{O}_2 : \text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$$

$$\text{Bond order} = \frac{8-4}{2} = 2$$

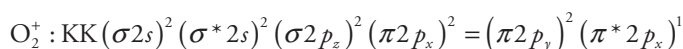
The bond order of two denotes that the oxygen molecule has a double bond (one σ and other π). It has two unpaired electrons in $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals, which makes the molecule paramagnetic. All the above facts have been proved experimentally. The bond dissociation energy of O_2 molecule is 495 kJ mol^{-1} and the bond length is 121 pm.

Comparison of O_2 , O_2^+ and O_2^- species

8. **Oxygen molecule ion (O_2^+)** When one electron is removed from O_2 molecule, O_2^+ ion is formed. The electron will be lost from antibonding MO, that is, $\pi^* 2p_x$ or $\pi^* 2p_y$



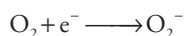
The electronic configuration of O_2^+ is



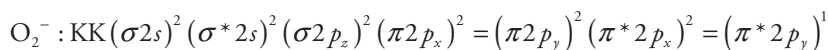
$$\text{Bond order} = \frac{8-3}{2} = \frac{5}{2} = 2\frac{1}{2}$$

The bond order of O_2^+ ion is greater than the bond order of O_2 molecule; therefore, the bond strength of O_2^+ will be more than that of O_2 molecule and its bond length will be less than the bond length of O_2 molecule.

Superoxide ion (O_2^-) Addition of one electron to O_2 forms O_2^- . This electron is added to either of the antibonding MO (s) ($\pi^* 2p_x$ or $\pi^* 2p_y$)



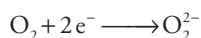
The electronic configuration of O_2^- is



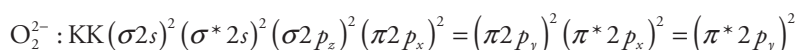
$$\text{Bond order} = \frac{8-5}{2} = \frac{3}{2} = 1\frac{1}{2}$$

The bond order of O_2^- ion is less than the bond order of O_2 molecule; therefore, its bond strength is less than O_2 molecule and bond length is larger.

Peroxide ion (O_2^{2-}) When two electrons are added to the antibonding orbitals of O_2 molecule, a peroxide ion O_2^{2-} is obtained.



The molecular orbital configuration of O_2^{2-} ion is



$$\text{Bond order} = \frac{8-6}{2} = 1$$

The bond order of O_2^{2-} ion is less than the bond order of O_2 molecule; therefore, its bond strength is less than O_2 molecule and bond length is larger.

Bond dissociation energies and bond lengths for O_2^+ , O_2 and O_2^- are in Table 10.3.

Table 10.3 Bond dissociation energies and bond lengths for O_2^+ , O_2 and O_2^-

Species	Bond order	Bond dissociation energy (kJ mol^{-1})	Bond length
O_2^+	$2\frac{1}{2}$	625	112 pm
O_2	2	495	121 pm
O_2^-	$1\frac{1}{2}$	395	130 pm

The species O_2 , O_2^+ , O_2^- and O_2^{2-} can be arranged as

Bond dissociation energy $\text{O}_2^+ > \text{O}_2 > \text{O}_2^- > \text{O}_2^{2-}$

Bond length $\text{O}_2^{2-} > \text{O}_2^- > \text{O}_2 > \text{O}_2^+$

9. **Fluorine molecule (F_2)** Fluorine atom with an electronic configuration of $1s^2 2s^2 2p^5$ has seven electrons in its valence shell. The molecular orbital electronic configuration of F_2 molecule is

$$\text{F}_2 = \text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$$

$$\text{Bond order} = \frac{8-6}{2} = 1$$

Thus, there is one σ bond in the molecule. The molecular orbital diagram shows that all the electrons are paired, making the molecule diamagnetic. Its diamagnetic behavior has been proved experimentally. The bond dissociation energy is found to be 155 kJ mol^{-1} and bond length is 142 pm.

10. **Hypothetical neon molecule** Neon atom has the electronic configuration $1s^2 2s^2 2p^6$. The molecular orbital electronic configuration of neon molecule will be

$$\text{Ne}_2 : \text{KK}(\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2 (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2 (\sigma^* 2p_z)^2$$

$$\text{Bond order} = \frac{8-8}{2} = 0$$

Thus, Ne_2 molecule is non-existent.

Heteronuclear diatomic molecules

The electronegativities of the two combining atoms in heteronuclear diatomic molecules are different. When such molecules form molecular orbitals, the bonding molecular orbital lies closer to the atom with higher electronegativity and the antibonding molecular orbital lies closer to the less electronegative atom.

In homonuclear molecules, the energy of the combining orbitals is equal, hence they interact effectively; however, in heteronuclear molecules the energy of the combining atomic orbitals is different hence effective overlap is not possible. Let us discuss the electronic structure and molecular orbital diagrams for some heterogeneous diatomic molecules.

1. **Hydrogen Fluoride molecule, HF** The electronic configuration of hydrogen and fluorine atoms are

$$\text{H} = 1s^1$$

$$\text{F} = 1s^2 2s^2 2p^5$$

HF molecule is formed by the linear combination of the H(1s) atomic orbital and one of the F atomic orbitals. The $1s^2$ and $2s^2$ orbitals of fluorine do not take part in bonding because their energy is very low. Because of symmetry considerations, out of the three 2p orbitals, only $2p_z$ orbital is able to combine with an s orbital. Therefore, during the formation of HF molecule, the bonding occurs due to the overlap of H (1s) electrons and $2p_z$ electrons of F, and the other electrons of fluorine remain in atomic orbitals.

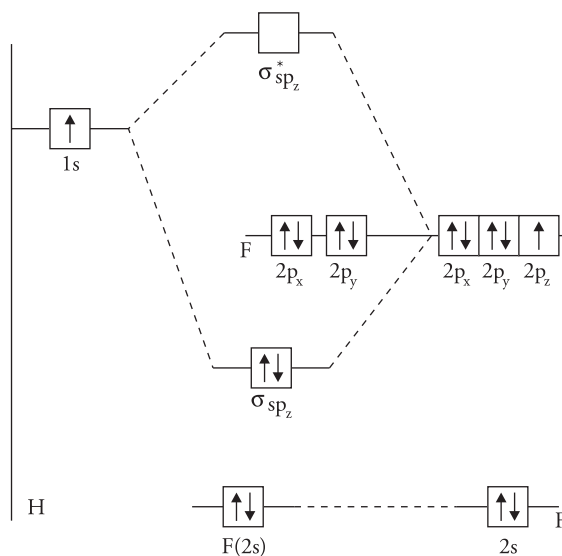


Figure 10.54 Molecular orbital energy level diagram for HF

The structure of HF molecule, therefore, may be written as

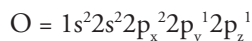
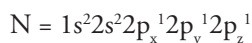


It is important to note that only one bonding molecular orbital σ_{2spz} is formed in HF molecule. This bonding MO contains two electrons. The remaining electrons remain in their atomic orbitals $2p_x$ and $2p_y$. The configuration of HF molecule closely resembles that of the neon atom ($1s^2 2s^2 2p^6$); however, as HF molecule is heteronuclear, the electrons are no longer shared equally between the two nuclei. The $\text{F}(2p_z)$ atomic orbital is contributing more than the $\text{H}(1s)$ orbital to the molecular orbitals. As seen in Figure 10.54 the molecular orbital has an energy that lies closer to that of $2p_z$ orbital of fluorine than to that of $1s$ orbital of hydrogen.

Similarly, in HCl, HBr and HI the electrons are shared unequally between the nuclei of their atoms. The chlorine, bromine and iodine atoms contribute, respectively, $3p_z$, $4p_z$ and $5p_z$ atomic orbitals in formation of these molecules.

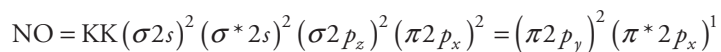
The molecular orbital diagram for HCl will be similar to HF.

2. **Nitric oxide molecule (NO)** The electronic configuration of N and O atoms are



The outer shell of nitrogen and oxygen have five and six electrons, respectively; thus, NO molecule has a total of 11 electrons. MO diagram for NO molecule is shown in Figure 10.55. The bonding MOs are closer to oxygen, as its electronegativity value is higher than nitrogen and antibonding MOs are closer to N atom.

The molecular orbital electronic configuration of NO molecule is



$$\text{Bond order} = \frac{8-3}{2} = 2\frac{1}{2}$$

The presence of an unpaired electron makes the NO molecule paramagnetic. The molecular orbital diagram of NO is similar to that of diatomic molecules such as O_2 or F_2 , except that the energy level of N and O are not the same.

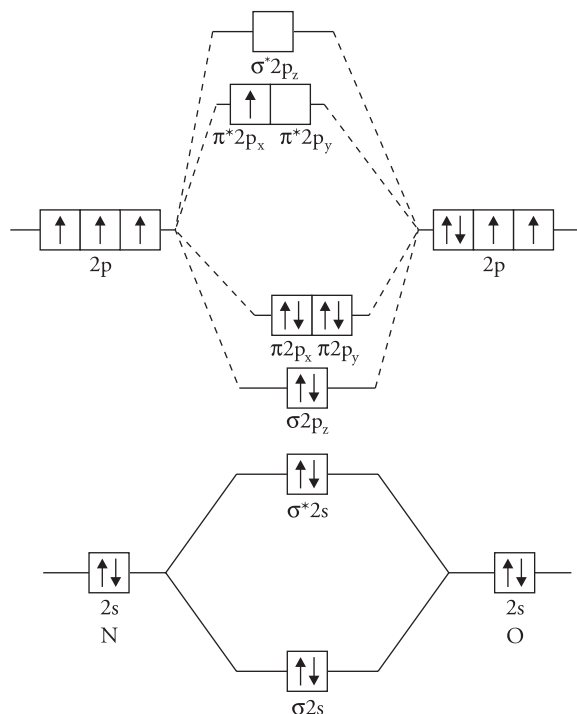


Figure 10.55 Molecular orbital diagram for NO molecule

3. **Carbon monoxide molecule CO** The electronic configuration of carbon and oxygen atoms are

$$\text{C} = 1s^2 2s^2 2p^2 \text{ and } \text{O} = 1s^2 2s^2 2p^4$$

The outer shell of carbon and oxygen have four and six electrons, respectively; thus the CO molecule has 10 electrons that occupy its molecular orbitals. The MO diagram for CO molecule may be drawn similar to NO molecule as shown in Figure 10.56. Then the molecular orbital configuration may be written as

$$\text{CO} = \text{KK} (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 (\pi 2p_y)^2$$

$$\text{Bond order} = \frac{8-2}{2} = 3$$

Thus, CO molecule has a triple bond (one σ and two π bonds). The molecule is diamagnetic, as there is no unpaired electron in it. Figure 10.56 gives the molecular orbital diagram of CO

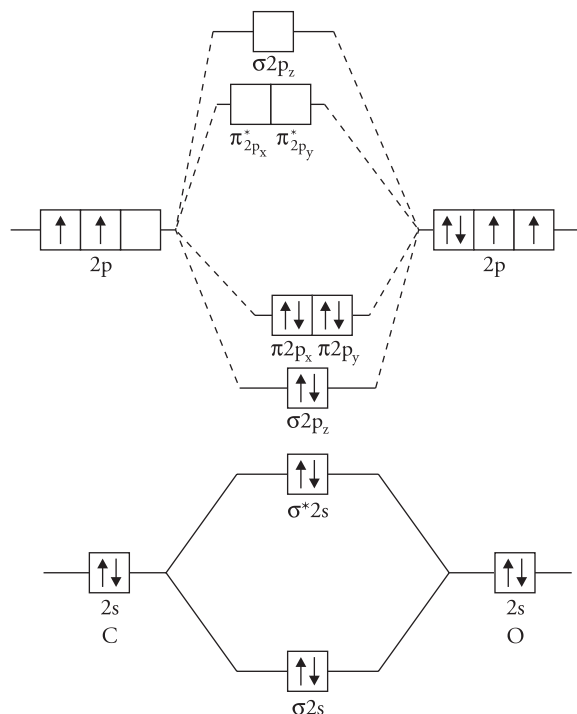


Figure 10.56 Molecular orbital diagram for CO molecule

10.13 Bonding in Metals – Metallic Bond

Metals have certain characteristic physical properties

1. They are good conductors of heat and electricity. The electrical conduction in metals is because of free electrons. It may be recalled that ionic crystals such as NaCl also conduct electricity, but in molten or fused state. In the solid state, ionic compounds conduct electricity to a very small extent because of the presence of defects in their crystals. The electrical conduction in metals is very different from the conduction of electricity in ionic solids.
2. Metals are lustrous. They have a shiny appearance.
3. Metals are malleable. This shows that they do not offer much resistance to deformation of the structure but that large cohesive forces hold them together.
4. The melting and boiling points of metals are high.
5. They are crystalline with high coordination number of 12 or 14.

All the above-mentioned properties of metals cannot be explained on the basis of normal ionic or covalent bonding.

Theories of Bonding in Metals

In a pure metal all the atoms are identical, hence they cannot be bound together by ionic bond that holds the cations and anions together in an ionic crystal. Ionic bond is formed when there is difference of electronegativity between the combining atoms. As metals have high melting points, they cannot be bound together by van der Waals forces. Ordinary covalent bonding cannot account for the high coordination number of 8–14. For example, Li has only one valence electron per atom (electronic configuration of Li is $1s^2 2s^1$). Hence, it cannot form covalent bonds with 8–14 near neighbors in the crystal. Moreover, metals retain their metallic properties in liquid state (for example, mercury), or when dissolved in suitable solvents (for example, solution of sodium in liquid ammonia). Any theory proposed to explain bonding in metals should also explain the great mobility of the electrons.

The bonding of metals in a metal crystal has been answered by the following theories

1. Electron Sea Model or Electron Pool Theory

The theory was proposed by Drude in 1900. He said that just as the molecules of a gas are free to move about, similarly a metal is a lattice with electrons moving through it. Lorentz (1923) refined the idea and said that the positively charged metal ions do not float randomly in a sea of electrons but occupy definite positions at measurable distances from each other in the crystal lattice. The valence electrons are not attached to any individual ion or pair of ions but they move about freely throughout the crystal lattice from one part to the other as the gas molecules move freely throughout the container. Thus, according to this theory, metallic solids can be considered as a collection of positive atomic cores immersed in a sea of mobile electrons. Metallic bond can be regarded as the force binding the metal ion and the mobile electrons within its sphere of influence.

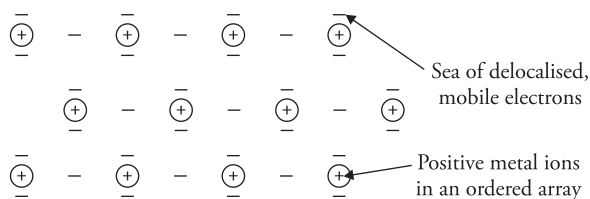


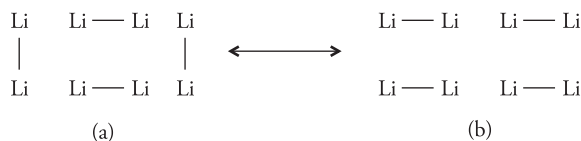
Figure 10.57 A schematic representation of sea of mobile electrons and positive metal cores

This theory could explain metallic lustre, thermal and electrical conductivity, malleability and ductility in metals but could not explain why electrical conductance of some metals increases with rise in temperature and why some metals do not conduct electricity and are classified as insulators.

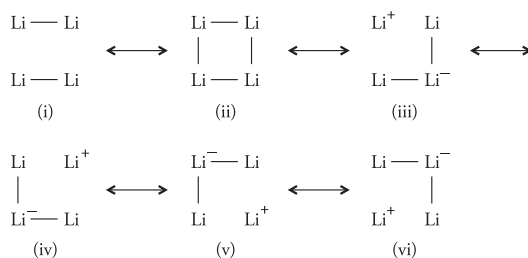
2. Valence Bond Theory

This theory was introduced by Pauling. This theory considers a metallic bond to be covalent in nature and believes that in a metallic structure the covalent bonds resonate between each atom and its nearest neighbor.

Let us consider the example of lithium metal. X-ray studies have proved that each atom has eight nearest neighbors. The electronic configuration of lithium is $1s^2 2s^1$. It has one electron in its valence shell. Hence, it is not possible for a lithium atom to form bonds with all its eight neighbors. This was explained by assuming that resonance takes place throughout the lithium solid. The resonating structures can be shown as follows



The stability resulting from the resonance shown above is less. Assuming unsynchronized resonance between the arrangement involving ions as well, we get the following structures that are relatively more stable.



Structures (iii), (iv), (v) and (vi) contain lithium atom with a negative charge bonded to two other lithium atoms by covalent bonds. This can be explained by considering the electronic configuration of lithium. It is $1s^2 2s^1 2p_x^0 2p_y^0 2p_z^0$. Lithium has three vacant 2p orbitals. The energy of these 2p orbitals is not very different from the energy of 2s orbitals; hence, the electron of 2s orbitals of one lithium atom can easily be transferred to one of the three 2p vacant orbitals of the other lithium atom to convert it to Li^- ion with the configuration $1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$. The lithium atom that gives electron becomes Li^+ and acquires the configuration $1s^2 2s^0$.

Thus, it is clear from the above discussion that a metal atom having vacant orbitals whose energy is almost equal to the energy of the outermost occupied orbital can form resonating structures.

The presence of ions could explain electrical conduction but this theory could not explain the following properties

- (i) Conduction of heat in solid state
- (ii) Metallic lustre
- (iii) Retention of metallic properties in liquid state or in solution.

3. Molecular Orbital Theory–Band Theory

This is the quantum mechanical treatment of the metallic crystal and may be considered as molecular orbital theory of covalent bonds extended to solids. Recall that the H_2 molecule has two $1s$ atomic orbitals that combine to form two molecular orbitals, a low energy bonding MO termed as σ orbital and a higher-energy antibonding MO expressed as σ^* . Bonding in Li_2 molecule occurs in a similar manner. The configuration of lithium is $1s^2 2s^1$. Ignoring the inner electrons, the $2s$ AOs on each of the two Li atoms combine to give two MOs. The valence electrons occupy the bonding molecular orbital and the antibonding molecular orbitals are vacant.

If we consider the formation of a lithium crystal by the addition of one lithium atom at a time then when three Li atoms combine three MOs will be formed (one bonding, one non-bonding and one antibonding). Four Li atoms combine to form four MOs (two bonding and two antibonding) and n Li atoms combine to form n MOs. A cubic crystal of lithium having about 10^{20} Li atoms combine to form an equal number of MOs, that is, 10^{20} MOs that are delocalised over all the atoms in the crystal.

As the number of molecular orbitals increases, the difference in energy level between the successive MOs decreases so that they almost merge to form a continuous band, the lower half of the band consists of bonding MOs and is filled whereas the upper half of the band consists of the anti-bonding MOs and is empty. Since the $2s$ band is only half filled, the electrons can move about freely and hence Li is a good conductor (Fig. 10.58).

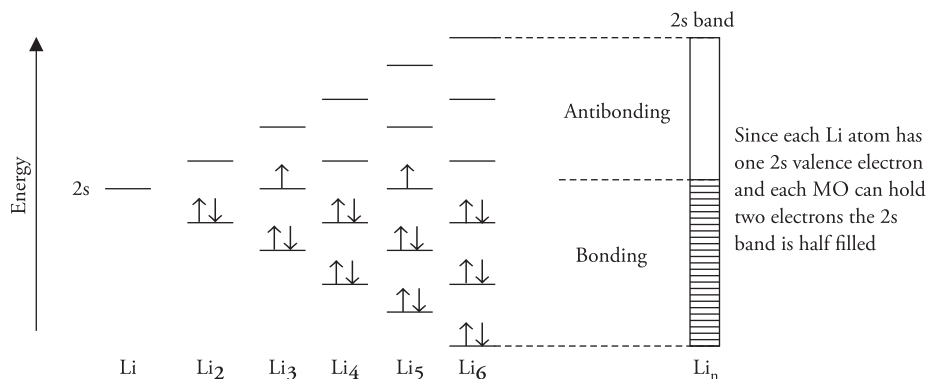


Figure 10.58 Illustration of band theory of solids using Li crystal

On the basis of the preceding discussion, one may assume that Be with electronic configuration $1s^2 2s^2$ and Mg with electronic configuration $[\text{Ar}]3s^2$ would be insulators as they have completely filled $2s$ and $3s$ bands, respectively. However this prediction is wrong because just as $2s$ and $3s$ orbitals overlap to form bands so also $2p$ and $3p$ orbitals overlap to form continuous bands. The upper part of $2s$ band overlaps with the lower part of $2p$ band and the resulting composite band is only partially filled. Similarly in Mg $3s$ and $3p$ overlap forming a partially filled band (Fig. 10.59). Hence Be and Mg are good conductors of electricity.

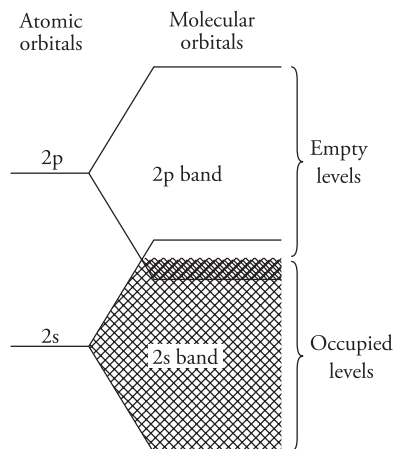


Figure 10.59 Overlapping band for beryllium

Energy Bands in Solids

There are three important energy bands in solids

- (i) Valence band
 - (ii) Forbidden band or forbidden energy gap
 - (iii) Conduction band
- (i) *Valence band (VB)* It is the highest occupied band below which all the bands are fully occupied. The valence band is occupied by the valence electrons that are shared in a covalent bond and transferred in an ionic bond. This band may be completely or partially filled depending upon the electronic configuration of the metal. For e.g., Li ($1s^2 2s^1$), Na ($1s^2 2s^2 2p^6 3s^1$) and Cu ($1s^2$ ----- $3d^{10} 4s^1$) have partially filled valence bands and Be ($1s^2 2s^2$) and Mg ($1s^2 2s^2 2p^6 3s^2$) have completely filled valence bands.
 - (ii) *Conduction band (CB)* It is lowest unoccupied band of MOs and is the empty band immediately above the valence band in solids. An electron in the valence band on acquiring enough additional energy becomes free and exists in the conduction band where it can move about freely as it is not tied to any given atom.
 In solids the conduction band is generally empty at O K but can be occupied by electrons at higher temperatures.
 - (iii) *Forbidden band or forbidden energy gap (E_g)* The gap between the valence band and the conduction band on the energy level diagram is known as the forbidden band or forbidden energy gap. Electrons may jump from valence band to conduction band, but they never exist in the forbidden band.

Application of Band Theory to Solids

On the basis of forbidden energy bands, all solids can be classified into insulator, semiconductor and conductor as given below:

- (i) **Insulator** In insulators the electrons are tightly bound to the parent atom and the forbidden energy gap (E_g) is very wide (5 – 10 eV). Even if there is high electric field, the electrons cannot jump from valence band to conduction band. However if very high energy is supplied or if the temperature is increased then some electrons may jump from valence band to conduction band making them good conductors at high temperatures. The resistivity of insulators is greater than 10^4 ohm.cm.
- (ii) **Semiconductors** Their properties lie between those of conductors and insulators. In case of semiconductors the forbidden energy band is very small (0.7 eV in germanium and 1.1 eV in silicon). The valence band is completely filled at 0 K and the conduction band has no electrons. If some energy is supplied to them, the electrons from valence band jump to the conduction band. As the temperature increases more and more electrons cross over to the conduction band and the conductivity increases. The resistivity of semiconductors is in the range of 10^{-3} to 10^3 ohm.cm.
- (iii) **Conductors** In conductors the valence band and conduction band overlap each other. There is no forbidden band in conductors. Hence electrons from the valence band enter the conduction band very easily and large numbers of free electrons are available for electrical conduction. Since there is no forbidden band in the conductors, so holes are not created and the electrical conduction is due to the flow of electrons only. Examples are silver, copper, etc. The electrical resistivity ranges from 10^{-9} to 10^{-3} ohm.cm and the electrical conductivity being reciprocal of resistivity ranges from 10^9 to 10^3 ohm⁻¹.cm⁻¹.

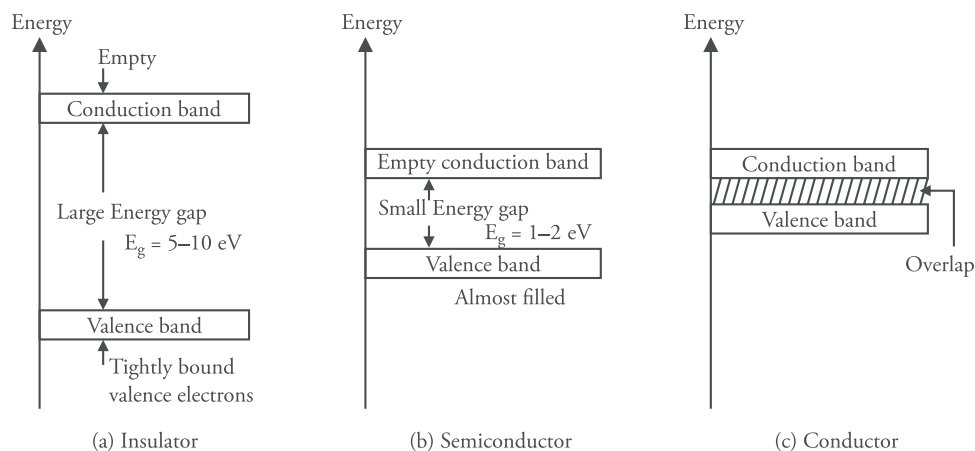


Figure 10.60 Energy bands in (a) Insulators (b) Semiconductors (c) Conductors.

Summary

- Atom consists of subatomic particles such as protons, neutrons and electrons. Many scientists like Thomson, Rutherford and Bohr attempted to explain the structure of atom.
- de Broglie suggested that light has dual nature : particle and wave nature. Properties such as photoelectric effect and black body radiation are explained by the particle nature, whereas wave nature explains reflection and diffraction of light.

He suggested $\lambda = \frac{h}{p}$

- Heisenberg's uncertainty principle states that simultaneous determination of both position and velocity of microscopic particle with absolute accuracy is impossible.

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

- Hybridisation is the intermixing of orbitals of different shapes, but almost equal energies to form the same number of new orbitals of equivalent energies and shape.
- Depending on the types of orbitals taking part in hybridisation, it can be sp^3 , sp^2 , sp , sp^3d , sp^3d^2 , sp^3d^3 and dsp^2 . Shapes of molecules depend upon their hybridisation types.
- Molecular orbital theory advocates that atomic orbitals of similar energy combine to form bonding, antibonding and non-bonding molecular orbitals.
- The electrons are filled in molecular orbitals in accordance to the Aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle.
- Molecular orbital theory explains the stability of molecules and their magnetic character.
- Metallic bonding is the bonding in metals. The theories of metallic bonding are electron sea model, valence bond theory and the band theory
- The band theory says that metals have three energy bands – conduction band, forbidden band and valence band. In metals valence and conduction band overlap, hence they are good conductors. In semiconductors the forbidden band is small $\sim 1\text{eV}$ and electrons easily move to conduction band, whereas in insulators the energy gap is $5\text{--}10\text{ eV}$, hence they do not conduct electricity.

Important relation in Quantum mechanics

- Schrodinger wave equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

- Condition for normalised wave equation $\oint \psi \psi^* d\tau = 1$
- Condition for orthogonal wave equation $\oint \psi \psi^* d\tau = 0$

- Laplacian operator ∇^2 is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

- Schrodinger equation in terms of Laplacian operator

$$\nabla^2\psi + \frac{8\pi^2m}{h^2}(E - V)\psi = 0$$

- Hamiltonian operator

$$\hat{H} = \left[\frac{-h^2\nabla^2}{8\pi^2m} + V \right]$$

- Schrodinger equation in terms of Hamiltonian operator :

$$\hat{H}\psi = E\psi$$

- Energy expression for particle in a box

$$E = \frac{n^2 h^2}{8ma^2}$$

where m = mass of the particle and 'a' is the length of the box $x = 0$ to $x = a$

- Total energy of particle in a three dimensional box:

$$E = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

- Spherical polar coordinate of cartesian coordinates x, y, z are

$$x = r \sin \theta \cos \phi$$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

- Huckel MO theory explains the formation of bonding and anti-bonding molecular orbitals in conjugated molecules. It is based on various approximations
- Huckel states that a compound with delocalised $(4n+2)$ π electrons will be aromatic where $n = 0, 1, 2, 3, \dots$. Hence a system having delocalised 2, 6, 10, 14, 18 π electrons would be aromatic.

Review Questions

1. Write the de Broglie's equation. How wave and particle nature of moving electrons are experimentally demonstrated?
2. Write short notes on
 - (a) Dual nature of radiation
 - (b) Heisenberg's uncertainty principle

- (c) Schrodinger wave equation
 - (d) Interpretation of wave functions.
3. Derive the Bohr's postulate of quantisation of angular momentum from de Broglie's relationship.
 4. Explain why is it impossible to measure simultaneously the position and velocity of a subatomic particle with accuracy. Why is Heisenberg's uncertainty principle ignored in everyday life?
 5. What is Schrödinger wave equation? What information is conveyed by Ψ and Ψ^2 ?
 6. What do you understand by hybridisation? Give an account of different types of hybridisation with suitable example.
 7. Discuss briefly the molecular orbital theory. Discuss the formation of HF and O₂ molecules on the basis of this theory.
 8. What do you understand by the linear combination of atomic orbitals (LCAO)? How are bonding and antibonding molecular orbitals formed. Also write down the conditions for the combination of atomic orbitals to form molecular orbitals.
 9. Draw the energy level diagram for O₂⁺ and calculate its bond order. Arrange O₂, O₂²⁻, O₂²⁺, O₂⁺ in the order of increasing bond lengths.
 10. On the basis of molecular orbital theory, explain the following
 - (i) Oxygen is paramagnetic
 - (ii) He₂ does not exist
 - (iii) N₂ is diamagnetic
 - (iv) Existence of H₂⁻ ion
 - (v) Be₂ does not exist
 11. Draw the energy level diagrams and calculate the bond order for N₂⁻, CO, NO, O₂⁺, He⁺, O₂²⁻ and O₂²⁺
 12. What is a metallic band? Explain the theories of bonding in metals.
 13. Explain the band theory. On the basis of this theory explain the conductivity in metals. Explain why the conductivity of semiconductors increases with rise in temperature.
 14. Solve the Schrodinger wave equation for a particle in a one dimensional box with zero potential energy inside the box. Normalise the wave function.
 15. Solve the Schrodinger wave equation for a particle in a three dimensional cubic box with edges of length *a* assuming that the potential is zero inside the box and infinite outside the box.
 16. Write the Schrodinger equation for hydrogen atom in terms of polar coordinates. Separate the resultant equation into three equations by separating the variable. Derive the quantum number *n*, *l* and *m* from the solution of wave function.
 17. Set and solve the Huckel secular equation for the molecules ethane, butadiene and benzene. Show the results on a MO diagram and calculate the resonance energy.
 18. Explain the Huckels concept of aromaticity.

Multiple Choice Questions

- According to Dalton's atomic theory, the smallest particle that is capable of independent existence is
 - Element
 - Atom
 - Molecule
 - Ion
- Which of the following is not a characteristic of Planck's theory of radiation
 - Energy is always associated with radiations.
 - The absorption and emission of energy occur continuously and not in small packets of energy called quanta.
 - The energy associated with a quantum of radiation is directly proportional to its frequency.
 - The emission and absorption of energy takes place in small packets called quanta.
- The equation $\lambda = \frac{h}{mv}$ was given by
 - Planck
 - de- Broglie
 - Heisenberg
 - Einstein
- The wave characteristic of electron was experimentally established by
 - de-Broglie
 - Schrodinger
 - Davisson and Germer
 - Neils Bohr
- Both particle and wave nature of a photon is established by
 - Interference
 - Reflection
 - Diffraction
 - $E = hv$
- Which among the following is diamagnetic
 - O_2
 - O_2^-
 - O_2^+
 - O_2^{2-}
- Germanium is an
 - Intrinsic semiconductor
 - Insulator
 - p-type semiconductor
 - n-type semiconductor
- An insulator is one which has
 - Empty energy bands
 - Half-filled energy bands
 - Completely filled energy bands
 - High energy difference between filled and empty bands
- Which among the following species does not exist
 - He_2
 - Be_2
 - Ne_2
 - All

10. The bond order of the given species are such that
 - (a) $O_2^- > O_2^+ > O_2^{2-} > O_2$
 - (b) $O_2^+ > O_2 > O_2^- > O_2^{2-}$
 - (c) $O_2 > O_2^{2-} > O_2^- > O_2^+$
 - (d) $O_2^{2-} > O_2 > O_2^+ > O_2^-$
11. Molecular orbitals are
 - (a) Monocentric
 - (b) Bicentric
 - (c) Polycentric
 - (d) None
12. In which of the following the central atom is sp^2 hybridised
 - (a) PCl_3
 - (b) SO_3
 - (c) BF_3
 - (d) NO_3^-
13. Which type of hybridisation is possible in square planar molecules
 - (a) sp^3d
 - (b) dsp^3
 - (c) dsp^2
 - (d) sp^3d^2
14. The correct expression for the Heisenberg's uncertainty principle is
 - (a) $\Delta x \times \Delta p \geq \frac{h}{4\pi}$
 - (b) $\Delta x \times \Delta p \leq \frac{h}{4\pi}$
 - (c) $\Delta x \times \Delta p = \frac{h}{4\pi}$
 - (d) $\Delta x \times \Delta p = 0$
15. Molecular orbital theory was proposed by
 - (a) Pauling and Slater
 - (b) Hund and Mulliken
 - (c) Davisson and Germer
 - (d) Neils Bohr
16. The structure of atom was first explained on the basis of the quantum theory by
 - (a) Rutherford
 - (b) Bohr
 - (c) Davisson and Germer
 - (d) Einstein
17. Which of the following molecular orbitals has the lowest energy
 - (a) $\sigma 2p_z$
 - (b) $\pi^* 2p_y$
 - (c) $\sigma^* 2p_z$
 - (d) $\sigma^* 2s$
18. The compound having pentagonal bipyramidal geometry with two types of bond angle is
 - (a) BrF_5
 - (b) ClF_3
 - (c) IF_7
 - (d) ClF_5
19. Which of the following molecules is diamagnetic
 - (a) Li_2
 - (b) B_2
 - (c) C_2
 - (d) O_2

20. Bonding in metals has been explained by the
 (a) Electron pool theory
 (b) Valence band theory
 (c) Molecular orbital theory (band theory)
 (d) All the above
21. Which of the following is the Schrodinger equation
 (a) $E = h\nu$ (b) $E = mc^2$
 (c) $H\psi = E\psi$ (d) $\frac{-h^2}{2m}\nabla^2$
22. A wave function is said to be normalised if it satisfies the condition
 (a) $\oint \psi \psi^* d\tau = 1$ (b) $\oint \psi \psi^* d\tau = 0$
 (c) $\oint \psi \psi^* d\tau \neq 1$ (d) $\oint \psi \psi^* d\tau = \infty$
23. Which of the following is termed as the Hamiltonian operator \hat{H}
 (a) $\frac{-h^2\nabla^2}{2m}$
 (b) $\frac{-h^2\nabla^2}{8\pi^2m} + V$
 (c) $\frac{h^2}{8\pi} + V$
 (d) $\frac{h^2\nabla^2}{8\pi^2m}$
24. The total π electron energy E_π of 1,3-butadiene is
 (a) $4\alpha + 4.472\beta$ (b) $2\alpha + 2\beta$
 (c) $6\alpha + 6\beta$ (d) $4\alpha + 6.924\beta$
25. The delocalisation energy of benzene is
 (a) 2.694β (b) 0.472β
 (c) 3β (d) 2β
26. Expression for energy for a particle in a one dimension box is
 (a) $E = \frac{n^2 h^2}{ma^2}$ (b) $E = \frac{n^2 h^2}{8ma^2}$
 (c) $E = \frac{\pi^2 h^2}{8ma^2}$ (d) $E = \frac{h^2}{8\pi^2 m}$

where m is the mass of the particle and 'a' is the length of the box ($x = 0$ to $x = a$)

Solution

1 (b)	2 (b)	3 (b)	4 (c)	5 (a)	6 (d)	7 (a)	8 (d)
9 (d)	10 (b)	11 (c)	12 (c)	13 (c)	14 (a)	15 (b)	16 (b)
17 (d)	18 (c)	19 (a)	20 (c)	21 (c)	22 (a)	23 (b)	24 (a)
25 (d)	26 (b)						

Chapter 11

SOLID STATE

11.1 Introduction

Solids are substances that have a definite shape and volume. They are highly incompressible and rigid and have high mechanical strength. The atoms, molecules and ions constituting the solid are closely packed and held together by strong intermolecular forces. The constituent particles occupy fixed positions in the solid and cannot move about freely. They can only oscillate about their mean positions. A true solid is characterised by a sharp melting point, a characteristic heat of fusion, incompressibility and a definite three-dimensional arrangement.

11.2 Types of Solids

Solids are of two types – crystalline and amorphous.

Crystalline solids

In crystalline solids, the atoms, molecules or ions constituting the solid are arranged in a regular manner to form a characteristic three-dimensional pattern. The regular arrangement of atoms is repeated several times throughout the molecule. Crystalline solids have long-range order and the arrangement of particles is so regular that if the arrangement of one area is known, the arrangement of particles in the entire crystal can be predicted. Moreover, a crystalline solid has the same geometry irrespective of the source from which it is obtained. Some examples of crystalline solids are NaCl, KCl, etc.

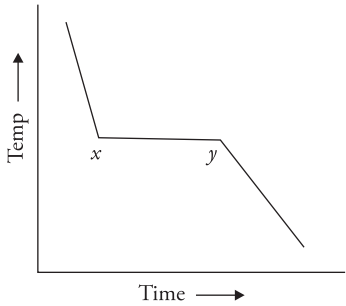
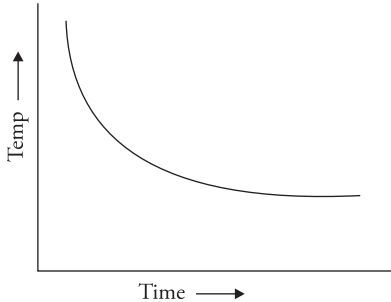
Amorphous solids

Amorphous (from the Greek word, *amorphos* meaning no form) solids have no regular arrangement of their atoms or molecules. In other words, they are characterised by a random arrangement of particles. They lack long-range order and can be regarded as supercooled liquids having structural units with a short-range order.

However, unlike liquids they have rigidity due to their enhanced viscosities and their constituent particles occupy fixed positions. Amorphous solids do not have sharp melting points – they melt over a range of temperature. Common examples of amorphous solids are glass, rubbers, plastics, etc.

Table 11.1 and Figure 11.1 explain the difference between crystalline and amorphous solids.

Table 11.1 Differences between crystalline and amorphous solids

S.No.	Crystalline solids	Amorphous solids
1	The constituent particles have a regular arrangement	They are characterised by random arrangement of the constituent particles
2	They have long-range order; the particle arrangement is same throughout the molecule	They have short-range order with small structural units
3	Crystalline solids are characterised by sharp melting points	Amorphous solids do not have a sharp and characteristic melting point; they generally melt over a range of temperature
4	They can be cleaved along definite planes	They cannot be cleaved along definite planes; they undergo irregular breakage when cut with a knife
5	They have different physical properties in different directions, i.e., they show anisotropy	Their physical properties are identical in all directions along any axis, i.e., they are said to show isotropy
6	Cooling curves have two breaks (x and y in the figure given below) corresponding to the beginning and end of the crystallisation process 	Cooling curve is smooth 
7.	Common examples include NaCl, KCl, sugar, diamond	Glass, rubber, plastics and polymers of high molecular weights are the common examples of amorphous solids

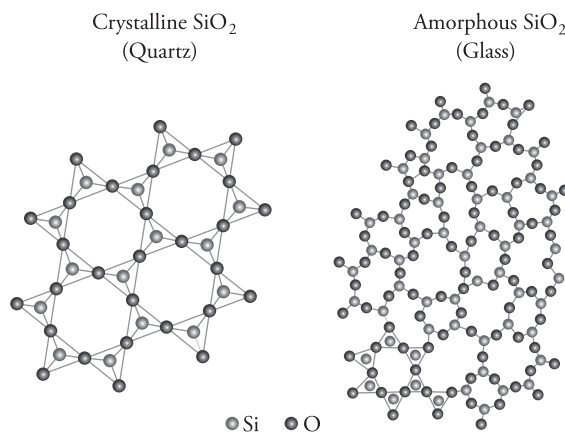


Figure 11.1 Crystalline and amorphous solids

Based on the nature of the intermolecular forces between the particles constituting the solid, all solids can be subdivided into four classes.

- (i) *Molecular solids* In molecular solids, molecules are the structural units. They are held together by weak van der Waals forces. The other forces between the molecules are hydrogen bonds, London dispersion forces and dipole–dipole interactions. They are fairly soft and have poor thermal and electrical conduction, for example, solid carbon dioxide, ice and iodine.
- (ii) *Ionic solids* Ionic solids are made up of positively and negatively charged ions. These ions are arranged in a regular fashion throughout the crystal and are held together by strong electrostatic forces of attraction. They are hard, brittle and have high melting and boiling points. Examples: NaCl, KCl, NaNO_3 , LiF and Na_2SO_4 .
- (iii) *Covalent solids* Covalent solids are made up of atoms that are bonded together by covalent bonds. In these solids, the atoms are interlinked by covalent linkages to form giant network solids. The atoms in these networks can be similar (as in diamond) or they can be different (as in silicon carbide). Since the atoms are held together by strong covalent bonds, they have high melting points; however, their thermal and electrical conductivity is poor. Examples include diamond, silicon carbide, quartz and silica.
- (iv) *Metallic solids* In metallic solids, the constituent particles are positive kernels immersed in a sea of mobile electrons. The forces of attraction present between the constituent particles are metallic bonds, which are very strong bonds; hence, these solids have high melting and boiling points. They are good conductors of heat and electricity due to the presence of mobile electrons. Metallic solids can be soft to very hard and are malleable and ductile. Examples include Cu, Fe, Al and Ni.

11.3 Crystal Lattice and Unit Cell

The atoms, ions or molecules constituting a crystalline solid have a definite orderly arrangement in three-dimensional space. When these particles (atoms, ions or molecules) are repeated again and again infinitely, then a crystal lattice or space lattice is formed. Thus, for a crystalline solid, a crystal lattice may be defined as a regular and repeating arrangement of particles (atoms, ions or molecules) in three-dimensional space. The positions occupied by the particles in this three-dimensional arrangement are termed as the lattice sites or lattice points.

Unit Cell

A careful look at the crystal lattice reveals that a group of lattice points is repeated over and over in the whole crystal lattice. This smallest repeating pattern is called the unit cell (Fig. 11.2).

Thus, a unit cell can be defined as:

The smallest portion of a crystal (space) lattice which produces the complete space lattice by repeating itself again and again.

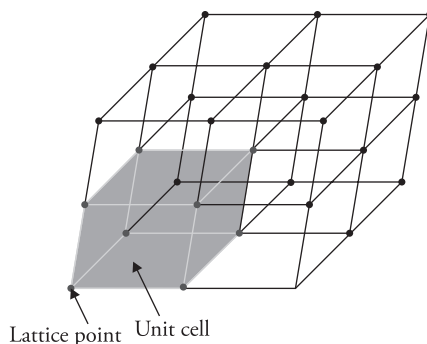


Figure 11.2 Representation of space lattice and unit cell

In order to describe a unit cell, the following has to be known:

- (i) The length of the edges (a , b and c) of the unit cell.
- (ii) The angles α , β and γ between the edges a and b , c and b , and a and c , respectively.

The dimensions (i) and (ii) are together called the unit cell parameters (Fig. 11.3).

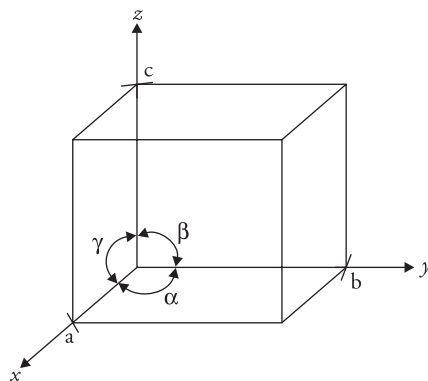


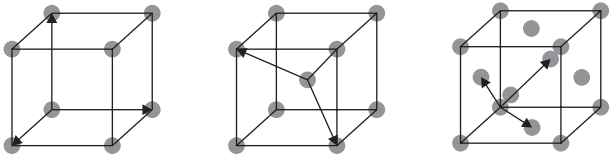
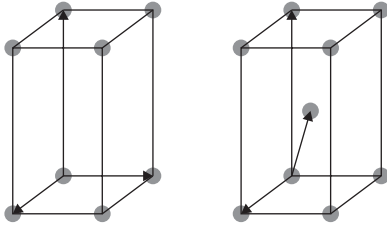
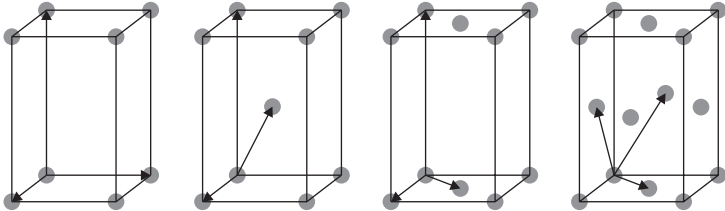
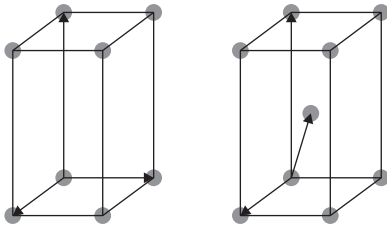
Figure 11.3 Representation of dimensions of a unit cell

11.4 Bravais Lattice

Considering the unit cell parameters (axial lengths and angles), seven crystal systems can be constructed. A. Bravais in 1848 showed that all possible three-dimensional space lattices are of 14 types. These are known as the Bravais lattices (Fig. 11.4) and are derived from the seven crystal systems mentioned in Table 11.2.

Table 11.2 Crystal systems

System	Axial distance characteristics	Axial angles	Examples
Cubic or regular	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl, CaF_2 , Cu_2O , ZnS, Pb, Ag, Au, Hg, alum, diamond
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	SnO_2 , TiO_2 , Sn, ZrSiO_4 , KH_2PO_4
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	PbCO_3 , BaSO_4 , K_2SO_4 , KNO_3 , rhombic sulphur, CdSO_4 , AgBr
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, monoclinic sulphur, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	ZnO, CdS, HgS, graphite, ice, PbI_2 , Mg, Cd, Zn
Rhombohedral (or trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), NaNO_3 , magnesite, quartz, As, Sb, Bi

System	Bravais lattice
Cubic or regular $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	

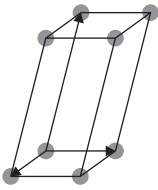
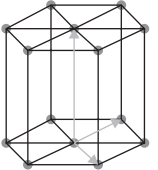
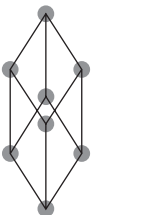
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Rhombohedral (or trigonal) $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	

Figure 11.4 Fourteen Bravais lattices

11.5 Types of Unit Cells and Number of Atoms per Unit Cell

There are three types of unit cells for cubic crystals – simple cubic, body centred cubic and face centred cubic.

- (i) *Simple cubic* In a simple cubic arrangement, the atoms, ions or molecules are present only at the corners of the cube (Fig. 11.5 a). The atom present at each corner is shared by 8 cubes and hence it contributes only 1/8 to each unit cell (Fig. 11.5 b). The total number of atoms per unit cell in a simple cubic arrangement is

$$8 \text{ corner atoms} \times 1/8 \text{ atom per unit cell} = 1 \text{ atom}$$

Thus, a simple cubic unit cell has one atom per unit cell. Only one metal, polonium has a simple cubic unit cell.

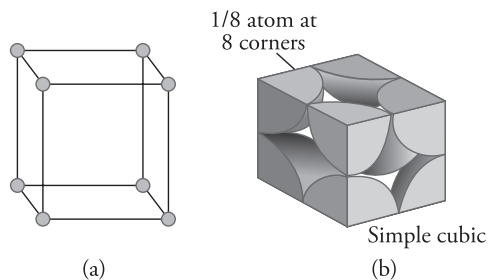


Figure 11.5 (a) Simple cubic arrangement. (b) Number of spheres per unit cell

- (ii) *Body centred cubic* A body centred cubic (BCC) has atoms, ions or molecules at all the corners as well as at the centre of the cube (Fig. 11.6 a). Each corner atom contributes $1/8$ to the unit cell; the atom at the centre belongs exclusively to the unit cell and is not shared by any other cube (Fig. 11.6 b). The total number of atoms per unit cell in a BCC arrangement can be determined as follows.

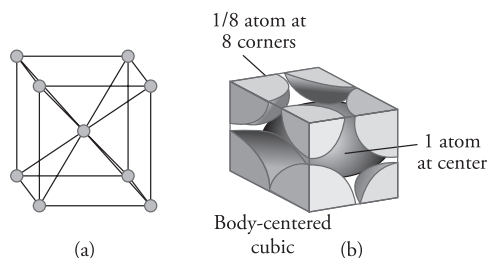


Figure 11.6 (a) Body centred cubic arrangement. (b) Number of spheres per unit cell

8 corner atoms \times $1/8$ atom per unit cell = 1 atom

Number of atoms at the centre of the cube = 1

\therefore Total number of atoms per unit cell in a BCC arrangement = $1 + 1 = 2$

Thus, a body centred cube has two atoms per unit cell.

- (iii) *Face centred cubic* A face centred cubic arrangement (FCC) is also termed as a cubic closed packed (CCP) arrangement. Apart from having atoms, ions or molecules at the corners, a face centred cube has atoms at the centre of each of the six faces (Fig. 11.7 a). The corner atom contributes $1/8$ to each unit cell and the atoms at the faces contribute $1/2$ to each unit cell (Fig. 11.7 b).

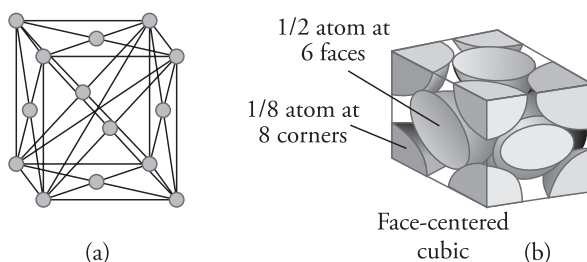


Figure 11.7 (a) Face centred cubic arrangement and (b) number of spheres per unit cell

The total number of atoms present per unit cell in an FCC or CCP arrangement is

8 corner atoms \times $1/8$ atom per unit cell = 1 atom

6 atoms at the faces \times $1/2$ atom per unit cell = 3 atoms

\therefore Total number of atoms per unit cell = $1 + 3 = 4$

Thus, a CCP or FCC arrangement has 4 atoms per unit cell.

Table 11.3 summarises the total number of atoms per unit cell for all three types of cubic crystals.

Table 11.3 Total number of atoms per unit cell

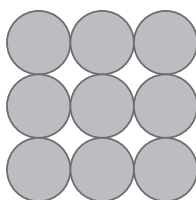
Unit cell	Number of atoms at the corner	Number of atoms at the faces	Number of atoms at the centre	Total number of atoms per unit cell
Simple cubic	$8 \times 1/8 = 1$	0	0	1
Body centred cubic	$8 \times 1/8 = 1$	0	1	$1 + 1 = 2$
Face centred cubic	$8 \times 1/8 = 1$	$6 \times 1/2 = 3$	0	$1 + 3 = 4$

11.6 Packing of Crystals

When crystal formation takes place, the constituent particles (atoms, ions or molecules) get closely packed together in such a way that they occupy the maximum available space. This type of packing is called *close packing*.

To understand packing of the constituent particles of crystals, it is assumed that all the spheres are of equal size. The packing of spheres takes place as follows.

- (i) *Simple cubic packing* It is the simplest possible arrangement of atoms. The atoms in the first layer are placed side by side. The atoms of the next layer are placed directly above the atoms of the first layer. Each atom is in direct contact with six atoms in its close vicinity (four in its plane, one atom in the layer above it and one in the layer below it (Fig. 11.8). *The number of atoms (spheres) touching a given sphere is called its coordination number*. Thus, the coordination number of each atom in simple cubic or primitive cubic packing is six. This arrangement of atoms is not very compact. Among metals, only polonium is reported to have this type of crystal lattice.

**Figure 11.8** Simple cubic packing

- (ii) *Body centred cubic (BCC)* In this type of packing, the spheres in the first layer are arranged like the spheres in simple cubic packing. However, the spheres of the second layer are not placed directly above the spheres of the first layer; rather they fit into the holes between adjacent spheres of the first layer (Fig. 11.9). Similarly, the spheres of the third layer fit into the holes between adjacent spheres of the second layer. The third layer is exactly similar to the first layer. Each atom touches four atoms in the layer above it and four in the layer below its plane. Thus, the coordination number of a body centred cubic is eight. Metals like Li, Na and K crystallise into a BCC arrangement.

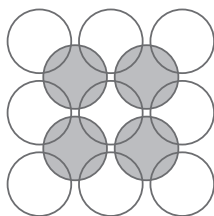


Figure 11.9 Body centred cubic packing. The second layer (shaded) is placed over holes in the first layer and the third over the holes in the second

- (iii) *Hexagonal closed packing (HCP)* In this type of packing, the atoms in the first layer have a hexagonal arrangement in which each sphere has six spheres in its immediate vicinity (Fig. 11.10 a). There are two types of voids in the first layer. They are marked as 'a' and 'b' (Fig. 11.10 b). All the voids are equivalent but the atoms of the second layer are placed either on the voids marked 'a' or on the voids marked 'b' (Fig. 11.10 c). It may be noted that since the atoms are much closer to each other, it is not possible to place atoms on both types of voids.

When the third layer of atoms is to be placed, they may be placed on the voids on the second layer (marked 'c'). In this arrangement, the spheres of the third layer lie directly above those of the first layer. In other words, the third layer becomes exactly identical to the first layer. This type of packing is termed as ABABA arrangement. It can also be called the hexagonal closed packing abbreviated as HCP (Fig. 11.11). Metals having hexagonal closed packing structures are Ba, Co, Mg and Zn.

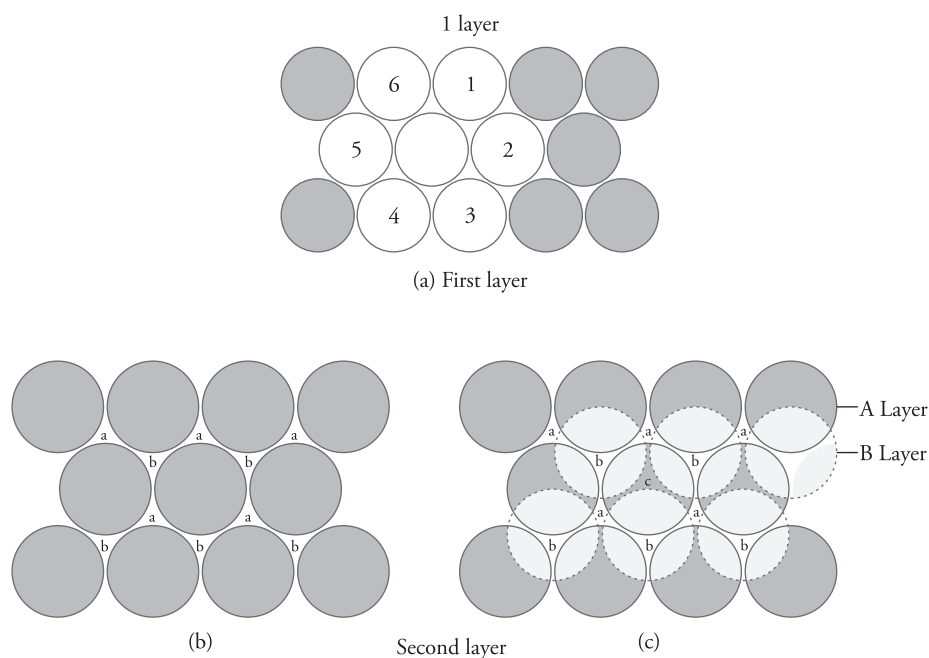


Figure 11.10 Arrangement of atoms in a hexagonal closed packing arrangement

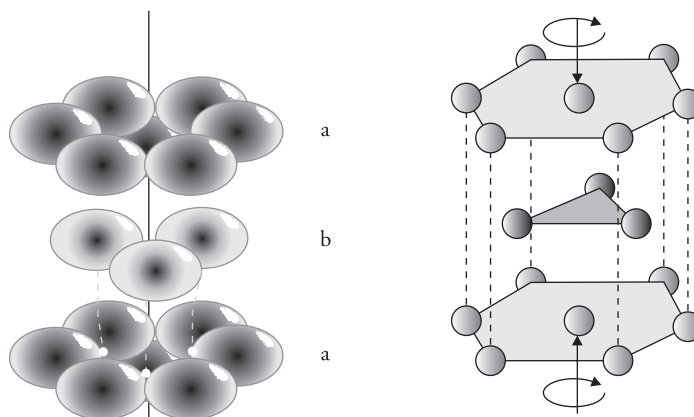


Figure 11.11 Hexagonal closed packing

- (iv) *Cubic closed packing (CCP or FCC)* An alternative way to pack the atoms of the third layer is to place them over voids marked 'a' (unoccupied voids of the first layer). This gives rise to a new layer labelled as 'c'. In this type of arrangement, the atoms of the fourth layer will correspond to those in the first layer (Fig. 11.12). This gives the ABCABCA type of arrangement. It is also known as cubic closed packing (CCP) or face centred packing (FCC) arrangement.

The coordination number in both HCP and FCC packing is 12 (six atoms in its own layer, three atoms in the layer above it and three in the layer below it). Metals like Ag, Au, Ca, Co, Cu and Ni have CCP structures.

Table 11.4 summarises the properties of the different types of packing in crystals.

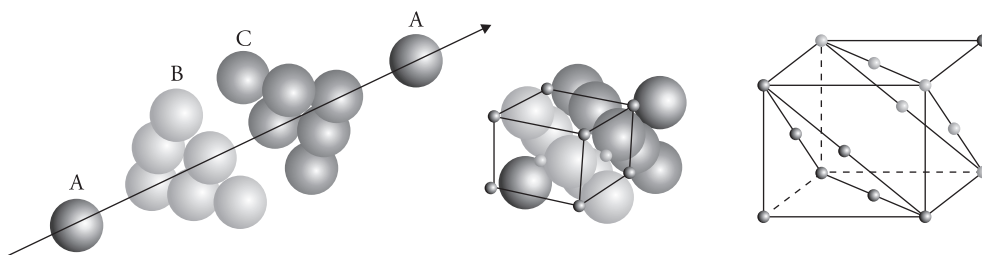


Figure 11.12 Cubic closed packing \equiv Face centred cubic

Table 11.4 Properties of different packing of crystals

Packing type	Coordination number	Packing efficiency (%) (explained later in this chapter)
Simple cubic (SC)	6	52
Body centred cubic (BCC)	8	68
Hexagonal closed packing (HCP)	12	74
Cubic closed packing (FCC)	12	74

11.7 Interstitial Sites or Interstitial Voids

Interstitial sites or interstitial voids are the vacant spaces left between atoms or spheres when they crystallise to form a crystal lattice. These are of two types – tetrahedral and octahedral.

- (i) *Tetrahedral void* In the closed packing of spheres, the atoms or spheres of the first layer are packed such that three spheres touch each other. The sphere of the second layer occupies the void or space between the spheres of the first layer. This void, therefore, has three atoms at the base and one atom at the apex; hence, the arrangement of atoms around this void is tetrahedral. Therefore, it is termed as a tetrahedral site or a tetrahedral void (Fig. 11.13). It is important to note that the void does not have a tetrahedral shape; the atoms or spheres are arranged tetrahedrally around the void.

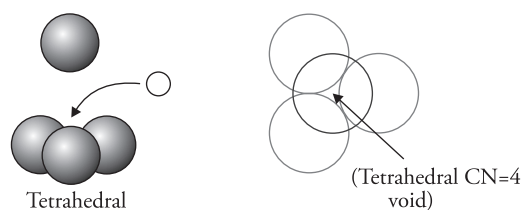


Figure 11.13 *Tetrahedral voids*

- (ii) *Octahedral void* When six spheres are arranged at the corners of two sets of equilateral triangles with their apices in opposite directions then the void or space formed at their centre is the octahedral void (Fig. 11.14). Hence, around an octahedral void six spheres are arranged at the vertices of a regular octahedron.

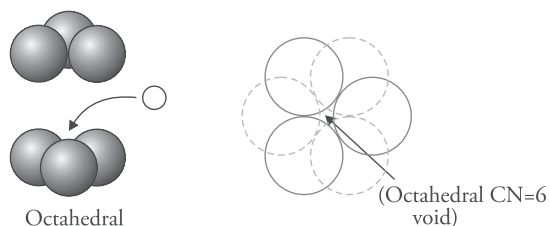


Figure 11.14 *Octahedral voids*

- (iii) *Number of octahedral and tetrahedral sites* In a closed packed structure, there are two tetrahedral sites for each sphere and one octahedral site for each sphere. If N is the number of spheres, then there are $2N$ tetrahedral voids and N octahedral voids.

11.8 Coordination Number and Radius Ratio

Ionic solids are made up of cations and anions having definite arrangements. Each cation is surrounded by a number of anions and vice versa. The arrangement of ions in a crystal and the

coordination number of the ions depend upon the radius of the ion with respect to the radius of the atoms or ions surrounding it. *This is called the radius ratio – it can be defined as the ratio of the radius of the cation to the radius of the anion.*

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{r^+}{r^-}$$

The radius ratio plays a vital role in determining the structure of the ionic solid. Ionic solids are held together by strong electrostatic forces. Those solids in which attraction between oppositely charged ions is maximum and repulsion between similarly charged ions is minimum will be stable. For an ionic crystal, the most stable arrangement will be one in which the anions are touching each other and the cation simultaneously (Fig. 11.15 a).

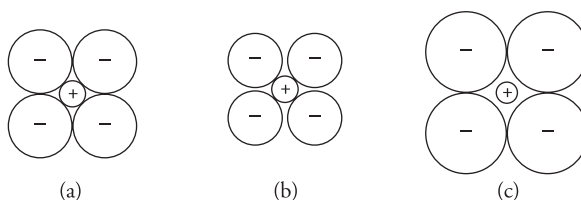


Figure 11.15 (a) Effect of change of size of anion (cation same) on stability of an ionic solid:
(b) stable and (c) unstable

Keeping the size of the cation same, if the size of the anion is reduced (i.e., radius ratio increases), the anions will not touch each other (Fig. 11.15 b). Hence, the structure will be unstable. To enable all the anions and cations to touch each other, more anions will have to be added, that is, the coordination number will increase.

Similarly, if the size of the anions is large keeping the size of the cations same (radius ratio decreases), the anions will touch each other but they will not be able to touch the cation (Fig. 11.15 c). The resulting structure will again be unstable. To stabilise the structure, the number of anions needs to be reduced, that is, the coordination number will decrease.

This is illustrated in Figure 11.16.

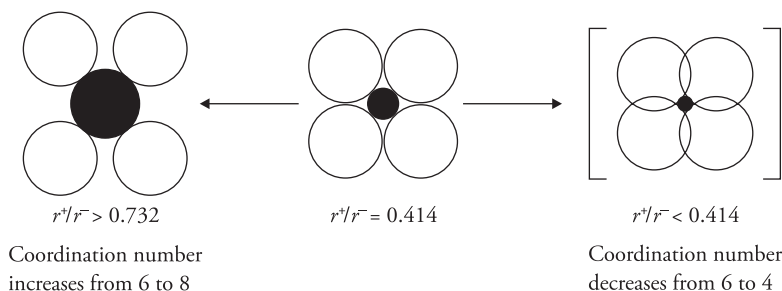


Figure 11.16 Effect of radius ratio on coordination number

The possible coordination and structural arrangements of anions around cations for different radius ratio values (r^+/r^-) are given in Table 11.5.

Table 11.5 Effect of radius ratio on coordination number

Radius ratio	Possible coordination number	Structural arrangement	Examples
0.0–0.155	2	Linear	HF_2^- (bifluoride ion)
0.155–0.225	3	Trigonal planar	B_2O_3 , BN
0.225–0.414	4	Tetrahedral	ZnS, SiO_4^{4-}
0.414–0.732	6	Octahedral	NaCl
0.732–1.0	8	BCC	CsCl

Solved Examples

- The radii of two ions X^+ and Y^- are 90 and 204 pm, respectively. In the close packed crystal of the compound XY, predict the coordination number of X^+ .

Solution

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{90}{204} = 0.44$$

Since the radius ratio is 0.44, which lies between 0.414 and 0.732, X^+ ions will have coordination number (CN) six.

- The radii of Zn^{2+} and S^{2-} ions are 74 and 184 pm, respectively. Predict the probable type of coordination of Zn^{2+} ions.

Solution

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}} = \frac{74}{184} = 0.402$$

Since the radius ratio lies between 0.225 and 0.414, the coordination number of Zn^{2+} is four.

- A solid AB crystallises into an NaCl type structure. If the radius of cation A is 100 pm, what is the radius of anion B?

Solution

Since AB has an NaCl type structure, its coordination number is six.

If CN = 6, the radius ratio lies between 0.414 and 0.732. Hence, the radius of B will lie between

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}}$$

$$0.414 = \frac{100}{x} \quad (x = \text{radius of anion})$$

$$x = \frac{100}{0.414} = 241.54 \text{ pm}$$

$$0.732 = \frac{100}{x}$$

$$x = \frac{100}{0.732} = 136.61 \text{ pm}$$

Hence, the radius of anion B ranges from 136.61 pm to 241.54 pm.

Practice problems

1. The radius of Na^+ ion is 95 pm and that of Cl^- ion is 181 pm. Predict whether the coordination number of Na^+ ion is 6 or 4. [Ans 6]
2. The ionic radii of Rb^+ , Br^- and I^- are 147, 195 and 216 pm, respectively. Predict the most probable type of coordination number of Rb^+ ion in RbBr and RbI on the basis of coordination number. [Ans 8 and 6, respectively]

11.9 Packing Efficiency and Atomic Radius

Packing efficiency is defined as the percentage or fraction of the total volume occupied by the particles (spheres) in a crystal lattice.

Let us calculate the packing efficiency and atomic radius for different types of unit cells.

(i) Simple cubic unit cell

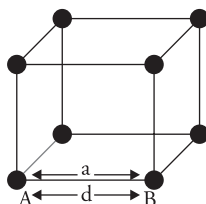
Suppose the edge length of the unit cell = a

or distance between nearest neighbour $d = AB$

Radius of the sphere = r

As the spheres are touching each other,

$$a = 2r, \text{ or } r = a/2$$



$$\text{Number of spheres per unit cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Volume of each sphere} = \frac{4}{3} \pi r^3$$

$$\text{Volume of the cube} = a^3 = (2r)^3 = 8r^3$$

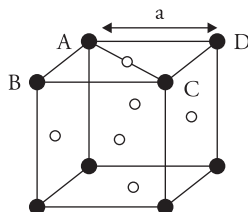
$$\text{Packing fraction} = \frac{\text{Volume of each sphere}}{\text{Volume of the cube}}$$

$$= \frac{\frac{4}{3} \pi r^3}{8r^3} = \frac{\pi}{6} = 0.524$$

Per cent of volume occupied = 52.4

(ii) *Face centred cubic (FCC) or cubic close packing (CCP)*

As the sphere on the face centre is touching the sphere at the centres, $AC = 4r$



In the right angle ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC = \sqrt{a^2 + a^2} = a\sqrt{2}$$

$$\therefore AC = 4r$$

$$\therefore 4r = a\sqrt{2}; a = \frac{4r}{\sqrt{2}} \text{ or } r = \frac{a}{2\sqrt{2}}$$

For an FCC arrangement, the number of spheres per unit cell = $8 \times 1/8 + 6 \times 1/2 = 4$

$$\text{Volume of each sphere} = \frac{4}{3} \pi r^3$$

$$\text{Volume of 4 spheres} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3$$

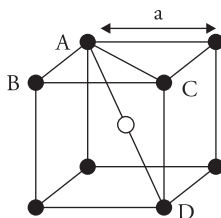
$$\text{Volume of the cube} = a^3 = \left(\frac{4}{\sqrt{2}} r \right)^3 = \frac{32}{\sqrt{2}} r^3$$

$$\therefore \text{Packing fraction} = \frac{\frac{16}{3} \pi r^3}{\frac{32}{\sqrt{2}} r^3} = \frac{\pi \sqrt{2}}{6} = 0.74$$

Per cent of volume occupied = 74

(iii) *Body centred cubic (BCC) arrangement*

As the sphere at the body centre touches the spheres at the corners, $AD = 4r$



AD is the body diagonal

In the right angle ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC = \sqrt{a^2 + a^2} = a\sqrt{2}$$

Now in the right angle ΔADC

$$AD^2 = AC^2 + DC^2$$

$$AD^2 = (a\sqrt{2})^2 + a^2 = 3a^2$$

$$AD = a\sqrt{3}$$

Also as seen above $AD = 4r$

Hence equating the two

$$4r = a\sqrt{3} \quad \text{or,} \quad r = a\sqrt{3} / 4 \quad \text{or} \quad a = 4r / \sqrt{3}$$

For a BCC arrangement, the number of spheres per unit cell $= 8 \times \frac{1}{8} + 1 = 2$

$$\text{Volume of each sphere} = \frac{4}{3} \pi r^3$$

$$\text{Volume of 2 spheres} = 2 \times \frac{4}{3} \pi r^3 = \frac{8}{3} \pi r^3$$

$$\text{Volume of the cube} = a^3 = \left(\frac{4r}{\sqrt{3}} \right)^3 = \frac{64r^3}{3\sqrt{3}}$$

$$\text{Packing fraction} = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} = \frac{\pi\sqrt{3}}{8} = 0.68$$

Percent of volume occupied = 68

The relation between radius of atom (r), edge length (a) and distance between nearest neighbour is summarised in Table 11.6.

Table 11.6 Relation between radius of atom (r), edge length (a) and distance between the nearest neighbour (d)

Unit cell	Distance between nearest neighbour (d)	Radius (r)	Packing fraction
Simple cubic	a	$a/2$	52.4%
Face centred cubic	$\frac{a}{\sqrt{2}}$	$\frac{a}{2\sqrt{2}}$	74%
Body centred cubic	$\frac{\sqrt{3}}{2}a$	$\frac{\sqrt{3}}{4}a$	68%

Solved examples

1. Iron crystallises into a body centred cubic structure. Calculate the radius of an iron atom if the edge length of a unit cell is 286 pm.

Solution

Edge length $a = 286$ pm

For a body centred cubic structure, radius of atom

$$r = \frac{\sqrt{3}}{4}a$$

$$\frac{\sqrt{3}}{4} \times 286 = 123.8 \text{ pm}$$

2. Xenon crystallises into a face centred cubic lattice. The edge of the unit cell is 620 pm. Find the distance with the nearest neighbour and radius of the xenon atom.

Solution

Edge length $a = 620$ pm

For a face centred cubic lattice

Distance between nearest neighbour = $a/\sqrt{2}$

$$= \frac{620}{\sqrt{2}} = \frac{620}{1.414} = 438.5 \text{ pm}$$

Radius of the atom = $\frac{a}{2\sqrt{2}}$

$$= \frac{620}{2\sqrt{2}} = \frac{620}{2 \times 1.414} = 219.25 \text{ pm}$$

3. NH_4Cl crystallises into a body centred cubic lattice. It has an edge length of 400 pm. Calculate
- Distance between NH_4^+ and Cl^- , that is, the oppositely charged ions in the lattice.
 - If the radius of NH_4^+ ions is 160 pm, find the radius of Cl^- ion.

$$(a) \quad r_{\text{NH}_4^+} + r_{\text{Cl}^-} = \frac{1}{2} \text{ body diagonal} = \frac{1}{2} \sqrt{3} a$$

$$\text{or } r_{\text{NH}_4^+} + r_{\text{Cl}^-} = \frac{\sqrt{3} \times a}{2} = \frac{\sqrt{3} \times 400}{2}$$

$$= 346.4 \text{ pm}$$

$$r_{\text{NH}_4^+} = 160 \text{ pm} \quad r_{\text{Cl}^-} = 346.4 - 160 = 186.4 \text{ pm}$$

Practice problems

- CsCl has a BCC arrangement. The edge length of its unit cell is 400 pm. Calculate the inter-ionic distance in CsCl . [Ans 346.4 pm]
- If an atom has a radius of 220 pm and crystallises into a face centred cubic lattice, find the length of the side of the unit cell. [Ans 622.16 pm]

11.10 Calculation of Density of a Crystal from Its Edge Length

The density of a cubic crystal can easily be calculated if its edge length is known.

Let,

$$\text{Edge length} = a \text{ pm} = a \times 10^{-10} \text{ cm} = a \times 10^{-12} \text{ m}$$

$$\text{Volume of unit cell} = (a \times 10^{-10} \text{ cm})^3 = a^3 \times 10^{-30} \text{ cm}^3$$

$$\text{Density of unit cell} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} \quad (\text{i})$$

Mass of unit cell = Number of atoms in a unit cell \times mass of each atom

$$= z \times m$$

where z = Number of atoms in the unit cell and

m = Mass of each atom

$$\text{Mass of each atom, } m = \frac{\text{Atomic mass}}{\text{Avogadro's number}} = \frac{M}{N_0}$$

$$\text{Mass of unit cell} = z \times \frac{M}{N_0} \quad (\text{ii})$$

Substituting (ii) in (i), we get

$$\text{Density of unit cell} = \frac{z \times M}{N_0 \times a^3 \times 10^{-30}} \text{ g/cc}$$

Solved examples

1. Calculate the volume of a cubic unit cell, whose edge length is 0.4 nm.

Solution

$$\text{Volume} = a^3 = (0.4 \times 10^{-9})^3 = 0.064 \times 10^{-27} = 64 \times 10^{-30} \text{ m}^3$$

2. Chromium has a monoatomic body centred cubic structure with an edge length of 300 pm. Calculate its density if the molar mass of Cr = 52 g mol⁻¹. Avogadro number = $N_0 = 6.023 \times 10^{23}$ /mol.

Solution

$z = 2$ since the structure is BCC

$$a = 300 \text{ pm} = 300 \times 10^{-10} = 3 \times 10^{-8} \text{ m}$$

$$M = 52 \text{ g mol}^{-1}$$

$$N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$$

Density = ?

$$\text{Density}(\rho) = \frac{zM}{a^3 \times N_0}$$

$$= \frac{2 \times 52}{(3 \times 10^{-8})^3 \times 6.023 \times 10^{23}} \text{ g/cc} = 6.395 \text{ g/cc}$$

3. Sodium has a BCC structure with nearest neighbour distance 365.9 pm. Calculate its density (atomic mass of sodium = 23)

Solution

For a BCC structure, the relation between edge length (a) and distance with the nearest neighbour (d) is

$$d = \frac{\sqrt{3}}{2} a$$

$$a = \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm}$$

For BCC structure $z = 2$

For sodium $M = 23$

$$\therefore \text{Density } \rho = \frac{z \times M}{a^3 \times N_0} = \frac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.023 \times 10^{23} \text{ mol}^{-1})} = 1.0126 \text{ g cm}^{-3}$$

4. The density of KBr is 2.73 g cm^{-3} . The length of the unit cell is 654 pm. Show that KBr has an FCC structure ($N_0 = 6.023 \times 10^{23} / \text{mol}$, Atomic mass K = 39, Br = 80)

Solution

Given $\rho = 2.73 \text{ g cm}^{-3}$, $a = 654 \text{ pm} = 6.54 \times 10^{-8} \text{ cm}$

M (for KBr) = $39 + 80 = 119 \text{ g mol}^{-1}$, $N_0 = 6.023 \times 10^{23} \text{ mol}^{-1}$

$$\rho = \frac{zM}{a^3 \times N_0} \quad \text{or} \quad z = \frac{\rho \times a^3 \times N_0}{M}$$

$$\therefore z = \frac{2.73 \text{ g cm}^{-3} \times (6.54 \times 10^{-8} \text{ cm})^3 \times 6.023 \times 10^{23} \text{ mol}^{-1}}{119 \text{ g mol}^{-1}} = 3.86 \approx 4$$

\therefore Number of atoms per unit cell is 4, KBr has FCC structure.

5. Calculate the value of the Avogadro number from the following data: Density of NaCl = 2.165 g cm^{-3} , distance between Na^+ and Cl^- in NaCl = 281 pm.

Solution

NaCl has a face centred cubic structure. Therefore, the number of formula units or molecules per unit cell = 4

As the distance between Na^+ and $\text{Cl}^- = 281 \text{ pm}$,

\therefore edge length of the unit cell = $2 \times 281 = 562 \text{ pm}$

$$\rho = \frac{zM}{a^3 \times N_0} \quad \text{or} \quad N_0 = \frac{z \times M}{a^3 \times \rho}$$

$$N_0 = \frac{4 \times 58.5 \text{ g mol}^{-1}}{(562 \times 10^{-10} \text{ cm})^3 \times 2.165 \text{ g cm}^{-3}}$$

$$= 6.09 \times 10^{23} \text{ mol}^{-1}$$

6. An element A (atomic mass 100) of BCC structure has an edge length of 400 pm. Calculate the density of A and the number of units for 10 g of A.

Solution

$$\text{Edge length} = 400 \text{ pm} = 400 \times 10^{-10} \text{ cm}$$

$$\text{Volume} = (400 \times 10^{-10} \text{ cm})^3 = 6.4 \times 10^{-23} \text{ cm}^3$$

since A crystallises in BCC structure,

$$z = 2 \text{ atoms/unit cell}$$

$$\text{Atomic mass } (M) = 100 \text{ g mol}^{-1}$$

$$\text{Density} = \frac{z \times M}{a^3 \times N_0}$$

$$= \frac{100 \text{ g mol}^{-1} \times 2 \text{ atoms/unit cell}}{6.4 \times 10^{-23} \text{ cm}^3 \times 6.023 \times 10^{23} \text{ atoms mol}^{-1}} = 5.188 \text{ g cm}^{-3}$$

$$\text{Volume of 10 g of A} = \frac{\text{Mass}}{\text{Density}} = \frac{10}{5.188 \text{ g cm}^{-3}} = 1.9275 \text{ cm}^3$$

Number of unit cells in 1.9275 cm³ volume

$$= \frac{\text{Volume of substance}}{\text{Volume of unit cell}} = \frac{1.9275 \text{ cm}^3}{6.4 \times 10^{-23} \text{ cm}^3}$$

$$= 3.0 \times 10^{22} \text{ unit cells}$$

Practice problems

- Aluminium forms a face centred cubic lattice whose unit cell edge length is 404 pm. Find the density of aluminium. [Ans 2.72 g/cc]
- The density of a face centred cubic element (atomic mass = 60.2 amu) is 6.2 g cm⁻³. Calculate the length of the edge of the unit cell (Avogadro's constant = 6.023 × 10²³ mol⁻¹). [Ans 401 pm]
- An element of atomic mass 98.0 g mol⁻¹ occurs in an FCC structure. If the unit cell has an edge length of 500 pm and its density is 5.22 g cm⁻³, calculate the value of Avogadro's constant. [Ans 6.0 × 10²³ mol⁻¹]

4. A body centred cubic element of density 10.3 g cm^{-3} has an edge length of 314 pm. Calculate the atomic mass of the element (Avogadro's constant is $6.023 \times 10^{23} \text{ mol}^{-1}$).
[Ans 96.18 g mol^{-1}]
5. Calculate the density of Mo which forms a body centred cubic crystal in which the distance between the centres of the closest atoms is 274 pm. Atomic mass of Mo is 95.94.
[Ans Edge length = 3.164×10^{-8} ; density = 10.06 g cm^{-3}]

11.11 Braggs Law: X-Ray Study of Crystals

The internal structure of crystals and the arrangement of atoms inside the crystal can be studied with the help of X-ray diffraction. It is well known that when light falls on an object whose size range is similar to the wavelength of light, it is diffracted (Fig. 11.17). In solid crystals, atoms are arranged in a fairly regular pattern and the spacing of atoms/ions/molecules in crystals is comparable to the wavelength of X-rays. Hence X-rays are easily diffracted from these crystalline solids.

A beam of X-ray on entering a crystal such as NaCl gets scattered in all directions. The resulting waves undergo destructive interference in some directions resulting in intensity minima and constructive interference in other directions resulting in intensity maxima.

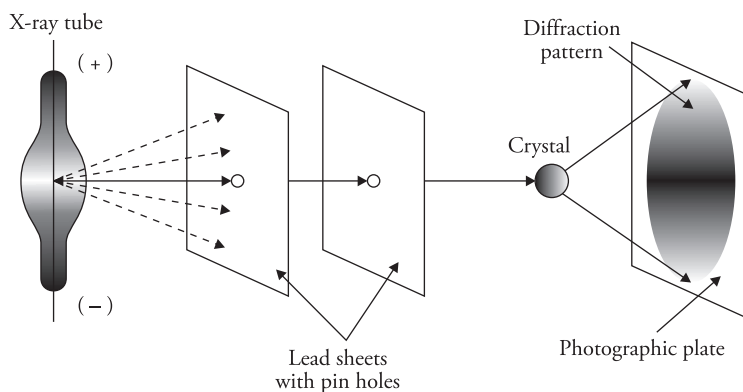


Figure 11.17 Experimental set up for X-ray diffraction of crystal

In the year 1913, Sir W H Bragg and his son Sir W L Bragg studied the phenomenon of diffraction of X-rays by crystals, for which, in 1915, they were awarded the Nobel prize in physics.

They gave Bragg's law, which states that 'when X-ray is incident on a crystal, it is diffracted from the atoms in the crystal planes and obeys the laws of reflection. If the angle of incidence is θ , then the angle of reflection will also be the same, that is, θ . Constructive interference will occur if the path difference between the two rays reflected from successive planes is an integral multiple of their wavelengths.

Bragg's equation can be derived as given below.

Let two parallel beams of X-rays P and Q fall on a crystal plane at an angle θ (Fig. 11.18). They will be reflected by the same angle. Let the wavelength of these X-rays be λ . The two successive

planes of the crystal are separated by a distance d . The X-ray beam P is reflected from the first plane and the beam Q enters the crystal and is reflected from the second plane. The ray Q reflected from the second plane travels an extra distance equal to $CB + BD$. Now according to Bragg's law, constructive interference will occur if this extra distance is equal to an integral multiple of the wavelength, that is,

$$CB + BD = n \lambda \quad (i)$$

where n is an integer (1, 2, 3, etc.)

Considering the geometry, we have

$$CB = BD = AB \sin \theta \quad (ii)$$

From eq. (i) and (ii), we have

$$n \lambda = 2 AB \sin \theta$$

$$\text{or } n \lambda = 2d \sin \theta$$

This is the Bragg's equation and is used to find the distance between successive planes in a crystal. If the value of $n = 1$, then the reflection corresponding to it is called the first order reflection. If $n = 2$, then the corresponding reflection is termed as the second order reflection and so on.

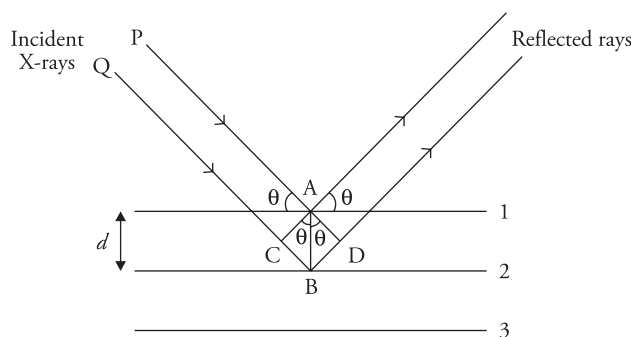


Figure 11.18 Bragg's diffraction

Solved examples

1. First-order X-ray ($\lambda = 154 \text{ pm}$) reflection maximum from a set of (200) planes of a body centred cubic lattice was observed at $16^\circ 6'$. Calculate the length of the edge of the unit cell.

Solution

For first order reflection $n = 1$, hence from Bragg's equation,

$$n \lambda = 2d_{200} \sin \theta \quad (\because n = 1)$$

$$\therefore d_{200} = \frac{\lambda}{2 \sin \theta} = \frac{154 \text{ pm}}{2 \sin 16^\circ 6'} = 277.67 \text{ pm}$$

$$a = 2 \times 277.67 \text{ pm} = 555.35 \text{ pm}$$

2. At what angle of incidence would the first order diffraction from the (110) plane of KCl be observed, using an X-ray of wavelength 154 pm? The dimension of the unit cell is 315 pm.

Solution

For the first order diffraction,

$$\lambda = 2d \sin \theta,$$

Given $\lambda = 154 \text{ pm}$, $d = 315 \text{ pm}$

$$\therefore \sin \theta = \frac{154}{2 \times 315} = 0.244 = \sin 14.1^\circ$$

Practice problems

- Calculate the distance between (100) planes of a crystal which exhibits first order reflection at an angle of incidence equal to 30° with X-rays of wavelength $2 \times 10^{-10} \text{ m}$.
[Ans $d = 2 \times 10^{-10} \text{ m}$]
- The distance between layers in an NaCl crystal is 282 pm. X-rays are diffracted from these layers at an angle of 23° . Assuming $n = 1$, calculate the wavelength of X-rays in nm.
[Ans 0.220 nm]

11.12 Structures of Simple Ionic Compounds

- Structure of sodium chloride (rock salt structure)*

A unit cell of sodium chloride is shown in Figure 11.19.

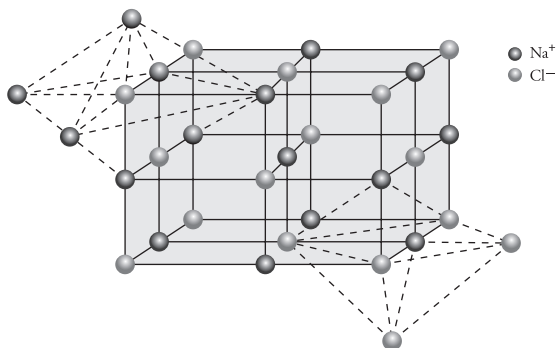


Figure 11.19 Structure of sodium chloride

Salient features

- It has a face centred arrangement (FCC or CCP). The Cl^- ions occupy the corners and faces of the cube. Na^+ ions occupy all the octahedral voids (i.e., Na^+ ions occupy the body centre and the edge centres).
- Since there is one octahedral void per atom in a CCP arrangement, the ratio of Na^+ and Cl^- ions is 1:1 and the formula of the compound is Na^+Cl^- .
- There are 8 Cl^- ions at the corners and 6 at the faces. Therefore, the number of Cl^- ions per unit cell is

$$8 \text{ corner ions contribute } \frac{1}{8} \text{ per unit cell} = 8 \times \frac{1}{8} = 1$$

$$6 \text{ ions at the faces contribute } \frac{1}{2} \text{ per unit cell} = 6 \times \frac{1}{2} = 3$$

$$\text{Total number of } \text{Cl}^- \text{ ions} = 1 + 3 = 4.$$

- Number of Na^+ ions can be calculated as follows:

$$12 \text{ ions at the edge centres contribute } \frac{1}{4} \text{ per unit cell} = 12 \times \frac{1}{4} = 3$$

$$\text{One at the body centre contributes fully} = 1 \times 1 = 1$$

$$\text{Total number of } \text{Na}^+ \text{ ions} = 3 + 1 = 4.$$

- Each Na^+ ion is surrounded by 6 Cl^- ions, which are disposed towards the corners of a regular octahedron. Similarly, each Cl^- ion is surrounded by six Na^+ ions. Therefore, the ratio of the coordination numbers of Na^+ and Cl^- ions in NaCl structure is 6:6. The sodium chloride structure is also called the rock salt structure.
- Other examples are halides of Li, Na, K, AgCl, AgBr, MgO, CaO, etc.

2. *Structure of zinc blende (ZnS)*

The unit cell of zinc blende is shown in Figure 11.20.

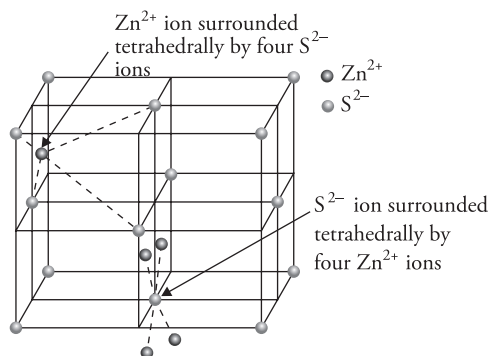


Figure 11.20 *Structure of zinc blende*

Salient features

- The S^{2-} ions adopt a cubic close packed arrangement. S^{2-} ions are present at the corners of the cube and at the centre of each face.

- Half of the tetrahedral voids are occupied by Zn^{2+} ions.
- There are two tetrahedral sites per atom. Since only half the tetrahedral sites are occupied by Zn^{2+} ions, therefore there is one Zn^{2+} ion for every S^{2-} ion. Hence, the compound has the formula ZnS .
- In the ZnS crystal, each zinc ion is surrounded by four sulphide ions, which are towards the corners of a regular octahedron. Similarly, each S^{2-} ion is surrounded by four Zn^{2+} ions, which are also arranged towards the corners of a regular tetrahedron.
- Number of S^{2-} ions per unit cell are

$$8 \text{ corner ions contribute } \frac{1}{8} \text{ per unit cell} = 8 \times \frac{1}{8} = 1$$

$$6 \text{ ions at the face centres contribute } \frac{1}{2} \text{ per unit cell} = 6 \times \frac{1}{2} = 3$$

$$\text{Total number of sulphide ions} = 1 + 3 = 4$$

The number of Zn^{2+} ions per unit cell will also be 4 because Zn^{2+} ions occupy half the tetrahedral sites

$$\text{Total number of ZnS per unit cell} = 4$$

Other examples of compounds adopting similar structures are CuCl , CuBr , CuI and AgI .

3. Structure of caesium chloride (CsCl)

The unit cell of CsCl is shown in Figure 11.21.

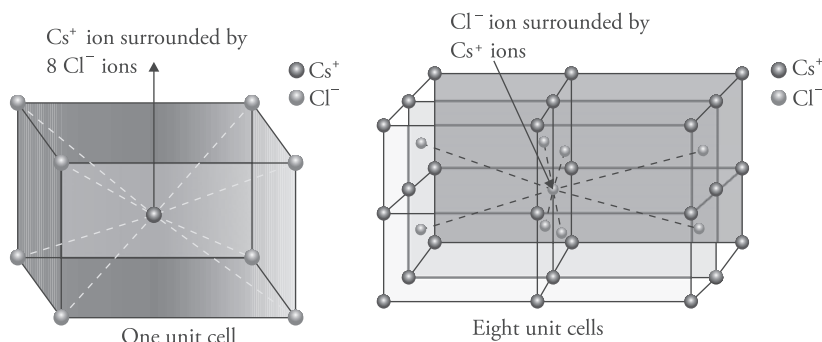


Figure 11.21 Structure of CsCl

Salient features

- It has a body centred cubic (BCC) arrangement in which Cl^- ions occupy the corners of the cube and the Cs^+ ion is present at the body centre of the cube.
- The crystal has a coordination number of 8:8 since each Cs^+ is surrounded by 8 Cl^- ions and each Cl^- ion is surrounded by 8 Cs^+ ions.

There are 8 Cl^- ions at the corners, therefore, the number of Cl^- ions per unit cell $= 8 \times \frac{1}{8} = 1$
 Cs^+ ion is in the body centre. Hence, the number of Cs^+ ions per unit cell $= 1 \times 1 = 1$,
 therefore, the total number of CsCl per unit cell $= 1$.

- Other compounds forming similar structures are CsBr, CsI, CsCN, TiCl, TiBr, etc.
4. *Structure of calcium fluoride (CaF_2 – Fluorite structure)*
The unit cell of calcium fluoride is shown in Figure 11.22.

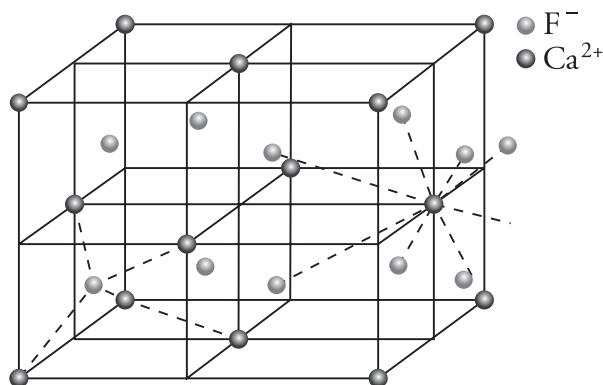


Figure 11.22 Structure of calcium fluoride

Salient features

- The Ca^{2+} ions adopt a CCP arrangement and are present at the corners and at the centre of each face.
 - The F^- ions occupy all the tetrahedral voids.
 - Since there are two tetrahedral voids per atom, for every Ca^{2+} ion, there will be two F^- ions. Thus, the formula of the compound will be CaF_2 .
 - In this structure, each F^- ion is surrounded by four Ca^{2+} ions, while each Ca^{2+} ion is surrounded by eight F^- ions. Thus, the ratio of the coordination numbers of Ca^{2+} and F^- ions is 8:4.
 - Number of Ca^{2+} ions per unit cell:

$$= 8 \text{ (corner ions)} \times \frac{1}{8} + 6 \text{ (face ions)} \times \frac{1}{2} = 1 + 3 = 4$$

As F^- ions occupy all the tetrahedral voids, the number of fluoride ions per unit cell = 8.
 Total number of CaF_2 per unit cell = 4
 - Other examples are BaF_2 , BaCl_2 , SrF_2 and SrCl_2
5. *Structure of sodium oxide (Na_2O) antifluorite structure*
The unit cell of sodium oxide is shown in Figure 11.23. The structure of Na_2O is similar to the structure of CaF_2 except that the position of anions and cations are reversed. O^{2-} ions adopt a CCP arrangement and Na^+ ions occupy all the tetrahedral voids. The coordination number of Na^+ ions is 4 and that of O^{2-} is 8. Thus, Na_2O has a 4:8 coordination. This structure is known as an antifluorite structure. Other compounds with this kind of crystal structure are Li_2O , K_2S , etc.

Table 11.7 provides a summary of all the structures learnt so far.

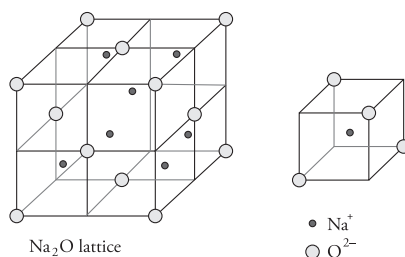


Figure 11.23 Structure of sodium oxide

Table 11.7 Summary of the structure of ionic compounds

Compound	Description	Coordination number	Number of formula units per unit cell	Other examples
NaCl (rock salt type)	Cl ⁻ CCP arrangement Na ⁺ all octahedral voids	Na ⁺ = 6 Cl ⁻ = 6	4	Halides of Li, Na, K, AgCl, AgBr, MgO, CaO
ZnS (zinc blende)	S ²⁻ CCP arrangement Zn ²⁺ half the tetrahedral sites	Zn ²⁺ = 4 S ²⁻ = 4	4	CuCl, CuBr, CuI, AgI, BeS
CsCl	Cl ⁻ simple cubic arrangement Cs ⁺ body centre of the cube	Cs ⁺ = 8 Cl ⁻ = 8	1	CsBr, CsI
CaF ₂ (fluorite type)	Ca ²⁺ CCP arrangement F ⁻ all tetrahedral sites	Ca ²⁺ = 8 F ⁻ = 4	4	SrF ₂ , BaF ₂ , CaF ₂
Na ₂ O (antifluorite type)	O ²⁻ CCP arrangement Na ⁺ all tetrahedral sites	Na ⁺ = 4 O ²⁻ = 8	4	Li ₂ O, K ₂ S

Effect of Temperature and Pressure on the Crystal Structure

High pressure increases the coordination number. At ordinary temperature and pressure, chlorides, bromides and iodides of lithium, sodium, potassium and rubidium crystallise into an NaCl type structure with coordination number 6:6.

On applying pressure, their coordination number increases to 8:8, that is, they are transformed into a CsCl type structure. If the CsCl structure is heated, it transforms into an NaCl type structure. NH₄Cl, NH₄Br and NH₄I transform from a CsCl structure to an NaCl structure at high temperature.

Solved examples

1. A unit cell consists of a cube in which there are anions (Y) at each corner and cations (X) at the centre of alternate faces of the unit cell. What is the simplest formula of the compound?

Solution

Number of anions (Y) per unit cell $= 8 \times \frac{1}{8} = 1$

Cations (X) are present at alternate faces, hence there are 3 cations each contributing $\frac{1}{2}$ to the unit cell. The number of cations (X) per unit cell $= 3 \times \frac{1}{2} = \frac{3}{2}$

Ratio of X:Y $= \frac{3}{2} : 1$

or X:Y = 3:2

Therefore, the simplest formula of the compound is X_3Y_2 .

2. In a cubic closed packed structure of mixed oxides, the lattice is made up of oxide ions. One-eighth of tetrahedral voids are occupied by divalent ions (A^{2+}) while one-half of octahedral voids are occupied by trivalent ions (B^{3+}). What is the formula of the oxide?

Solution

In a CCP arrangement, there is one octahedral void and two tetrahedral voids per atom.

Therefore, if the number of oxide ions (O^{2-}) per unit cell $= 8 \times \frac{1}{8} = 1$,

number of tetrahedral voids $= 1 \times 2 = 2$

\therefore Number of A^{2+} ions $= 2 \times \frac{1}{8} = \frac{1}{4}$

Number of octahedral voids $= 1 \times 1 = 1$

\therefore Number of B^{3+} ions $= 1 \times \frac{1}{2} = \frac{1}{2}$

Formula of the compound is $A_{1/4}B_{1/2}O$

The whole number formula of the compound $= AB_2O_4$

3. Two elements X and Y constitute a cubic solid. Y atoms are present at the corners of the cube and X atoms are present at the body centre. What is the formula of the compound? What are the coordination numbers of X and Y?

Solution

Number of Y atoms per unit cell $= 8 \times \frac{1}{8} = 1$

Number of X atoms per unit cell $= 1$

\therefore Formula of the compound $= XY$

\therefore The above structure is a CsCl type structure, its coordination number is 8:8.

Practice problems

1. If three elements A, B and C crystallise into a cubic solid lattice with atoms A occupying the corner, B the body (cube) centre and C the edges, what is the formula of the compound?
[Ans ABC_3]
2. A unit cell consists of a cube in which the atoms X are at the corners and the Y atoms occupy the face centre. X atoms are missing from 2 corners in each unit cell. Write the simplest formula of the compound.
[Ans XY_4]
3. A solid is made up of two elements P and Q. P atoms crystallises into a FCC arrangement and all the octahedral voids and alternate tetrahedral voids are occupied by Q. Write the formula of the compound.
[Ans PQ_2]

11.13 Imperfection in Solids

An ideal crystal (Fig. 11.24 a) is one in which all the constituent particles occupy their positions in the unit cell and throughout the whole crystal. Such ideal crystals exist only at absolute zero (0 K) temperature. At absolute zero, the crystal is highly ordered but above 0 K, they deviate from the perfectly ordered arrangement. The term *defect* or *disorder* or imperfection is used to denote departure from the perfectly ordered arrangement of the constituent particles. Imperfection results in change of properties.

Generally, there are two types of imperfections – electronic imperfections and atomic imperfections.

1. *Electronic imperfections*

These are defects in ionic crystals due to electrons. In an ideal crystal at 0 K, the electrons occupy the fully occupied highest energy states but at a temperature above 0 K, some of these electrons may occupy higher energy states. Electrons may be released from covalent bonds and they may become free to move. The bonds from which the electrons are removed become electron deficient and these are termed as holes. Free electrons and holes in the crystals are called electronic imperfections. The presence of free electrons and holes increases the conductivity of the crystal.

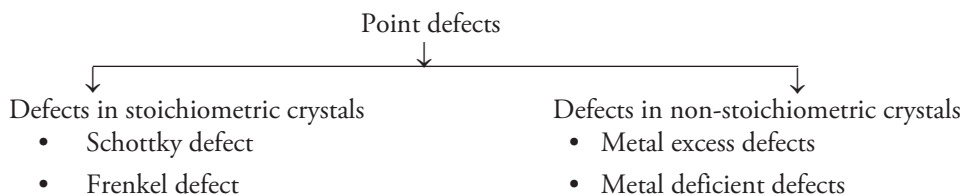
For example, in silicon and germanium, the concentration of electrons and holes will be equal. However, holes and electrons can be preferentially produced by adding trivalent impurity (e.g., B, Al, Ga) or pentavalent impurity (e.g., P, As) in Si or Ge crystal, which makes them semiconductors.

2. *Atomic imperfections*

Atomic imperfections are also termed as point defects and arise due to irregularity in the arrangement of atoms or ions in the crystal. Point defects may arise when either

- some constituent particles are missing from their position or
- the constituent particles shift from their positions and occupy interstitial spaces.

Point defects may be classified as follows:



Let us discuss them one by one:

A. *Point defects in stoichiometric crystals*

Stoichiometric compounds are those in which the number of positive and negative ions are exactly in the ratios as indicated by their chemical formulae.

To illustrate these defects, let us consider a crystal of the type AB having equal number of A^+ and B^- ions. In these compounds, two types of defects are generally observed – Schottky and Frenkel defects.

- (i) *Schottky defects* This defect was discovered by the German scientist Schottky in 1930. Schottky defects arise when some ions are missing from their lattice sites (Fig. 11.24 b). These unoccupied sites are called lattice vacancies or holes. To maintain electrical neutrality, the cations and anions are lost in pairs. As a result, the density of crystals is markedly lowered.

Such defects are common in crystals of NaCl, KCl, KBr and CsCl, where the size of the anion and the cation are almost similar.

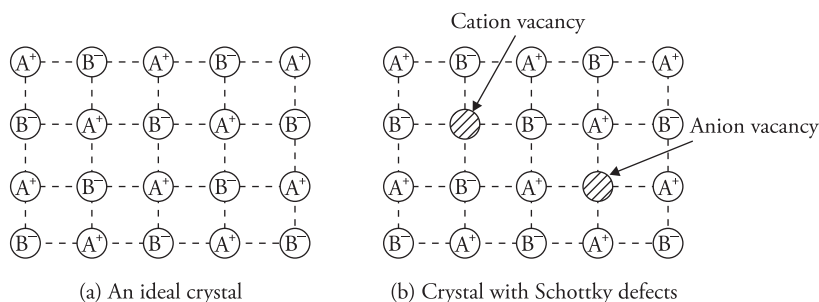
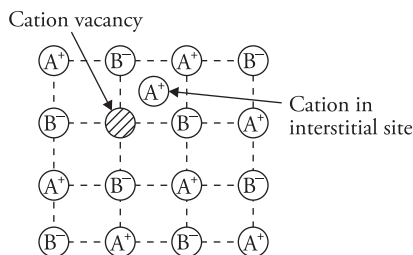


Figure 11.24 Arrangement of ions in (a) an ideal crystal and (b) a crystal with Schottky defect

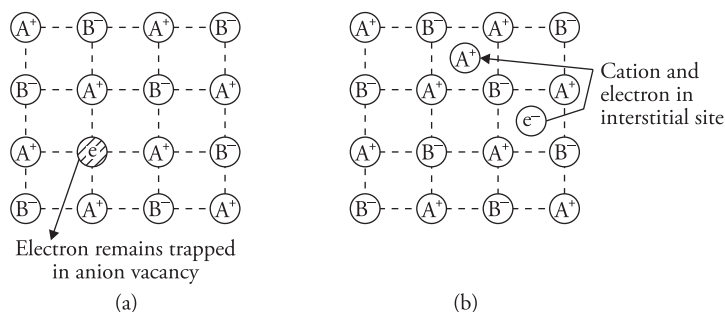
- (ii) *Frenkel defect* This defect was discovered by Russian scientist Frenkel in 1926. In this type of defect, the ion leaves the lattice point and occupies the interstitial site between the lattice points. As cations are small in size, they are generally displaced from their original position to adjacent voids (Fig. 11.25). This defect occurs in ionic crystals where the anion is much larger in size than the cation. Example: silver halides such as AgCl, AgBr and AgI where Ag^+ ions being much smaller than the halogen atom moves into the interstitial space. This defect does not affect the density of the crystal.

**Figure 11.25** Frenkel defect**B. Point defects in non-stoichiometric crystals**

Non-stoichiometric compounds are those in which the ratio of positive and negative ions present in the compound differs from that required by the ideal chemical formula of the compound. The defects in such crystals are called non-stoichiometric defects. They are of two types depending on whether the positive ions are in excess or the negative ions are in excess – *metal excess defects* and *metal deficient defects*, respectively.

(i) **Metal excess defects** In these defects, the positive ions are in excess. They can arise in two ways.

(a) **Anion vacancies** This arises when the negative ions are missing from the lattice sites. Absence of an anion leaves a vacancy that is occupied by a trapped electron (Fig. 11.26 a). The vacant sites occupied by trapped electrons are called F – centres. This type of defect is observed in crystals that are likely to have Schottky defects. For example, when alkali metal halide crystals are heated in an atmosphere of alkali metal vapours, the metal gets deposited on the surface of the alkali metal crystal. The halide ion moves to the surface and combines with the metal atoms. The electrons produced by the ionisation of the metal diffuse into the crystal and get trapped at the anion vacancies. This gives interesting properties to crystals. For example, the excess of potassium in KCl makes the crystal appear violet, excess lithium in LiCl makes the crystal appear pink.

**Figure 11.26** (a) Metal excess defects due to anion vacancy. (b) Metal excess defects due to extra cation

(b) **Excess cation occupying interstitial sites** In such type of defects, an extra cation is trapped in one interstitial site and an electron is trapped in the other interstitial site to maintain

electrical neutrality (Fig. 11.26 b). This defect is shown by crystals that are likely to develop Frenkel defects. An interesting example is zinc oxide. It loses oxygen reversibly at high temperature and turns yellow in colour. The excess Zn^{2+} ions are trapped in interstitial sites and an equal number of electrons in other sites to maintain electrical neutrality. The electrons increase the electrical conductivity.

Consequences of metal excess defects Crystals with metal excess defects are good conductors of electricity and are generally coloured. For example, non-stoichiometric sodium chloride is yellow.

(ii) *Metal deficient defects* In these defects, the number of positive ions is less than the number of negative ions. They arise in two ways.

(a) *Cation vacancies* The cation is missing from the lattice site (Fig. 11.27 a). To maintain electrical neutrality, the nearby cation gains an extra positive charge. This type of defect is possible where the metal ion exhibits variable valency like transition metals.

Examples include FeO, FeS and NiO.

In case of iron pyrites, two out of three ferrous ions in the lattice are converted to Fe^{3+} and the third Fe^{2+} may be missing from its lattice site. Therefore, the crystal contains Fe^{2+} and Fe^{3+} . This gives rise to exchange of electrons from one Fe^{2+} ion to an Fe^{3+} ion which increases the conductivity.

(b) *Extra anion occupying interstitial sites* In this case, an extra anion occupies the interstitial site (Fig. 11.27 b). In order to balance the charge, the charge on the adjacent cation increases. Negative ions are usually large; hence, it is difficult for them to occupy the interstitial sites. No crystal containing negative ions in interstitial spaces have been reported so far.

Consequences of metal deficient defects Crystals with metal deficient defects act as semiconductors. The conductivity arises due to movement of electrons from one ion to other. Substances where such types of movements occur are called p-type semiconductors.

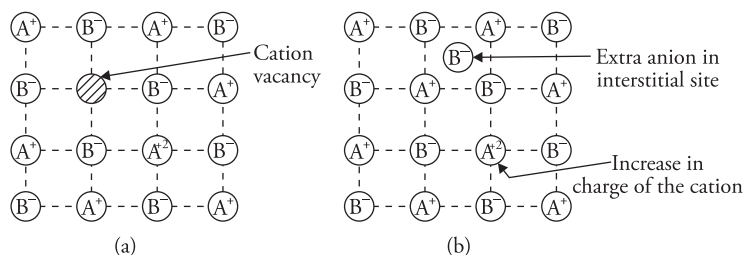


Figure 11.27 (a) Metal deficient defect due to cation vacancy. (b) Metal deficient defect due to extra anion

11.14 Semiconductors

Their properties lie between those of conductors and insulators. The classification of solids on the basis of band theory into insulators, conductors and semiconductors has already been discussed in Section 10.13. This section discusses the different types of semiconductors in detail.

Elemental Semiconductors

Elemental semiconductors are made of one type of element only, for example, silicon semiconductor has only silicon atoms and germanium semiconductor is made of germanium atoms only. They are of two types.

- (i) **Intrinsic semiconductor** They are extremely pure semiconductors (more than 99.99% pure). For example, silicon and germanium; they have four valence electrons. Their forbidden energy gap is about 1 eV. In such semiconductors, the energy gap is so small that even at ordinary temperatures the electrons possess sufficient energy to jump across the forbidden gap to the conduction band. On the removal of an electron from the valence band, a vacancy termed as 'hole' is created. The neighboring electrons in the valence band fill this hole and in turn leave behind a 'hole' in their place. Thus, when an electric field is applied to an intrinsic semiconductor, the electrons in the conduction band move towards the anode and the holes in the valence band move in the opposite direction, that is, towards the cathode. Hence, in an intrinsic semiconductor the charge is carried by electrons and holes in equal numbers (Fig. 11.28).

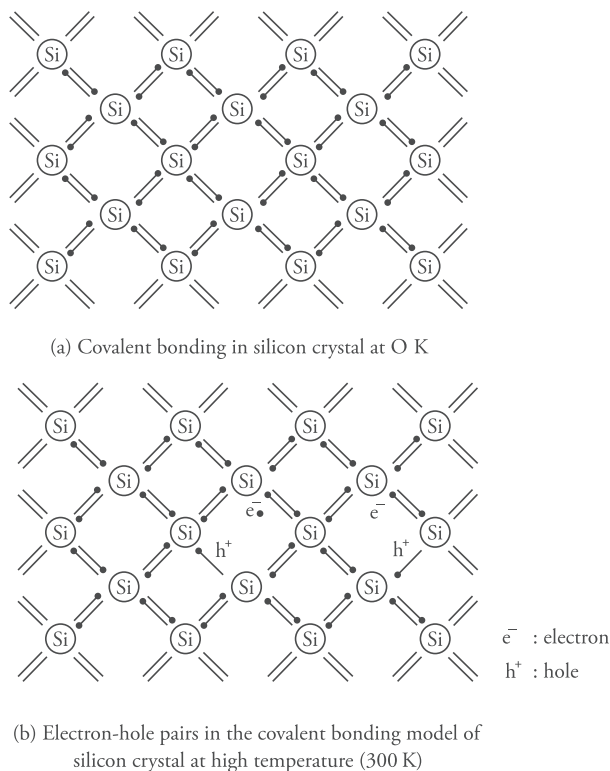


Figure 11.28 *Intrinsic semiconductor*

- (ii) **Extrinsic Semiconductors** They are intrinsic semiconductors (Si or Ge) in which impurity has been added to improve their conductivity (Fig. 11.29). The added impurity is called the dopant and the process is called doping. Extrinsic semiconductors can be of two types.

- (a) **n-type semiconductor** They are obtained by adding a pentavalent impurity (such as phosphorus, arsenic or antimony) to pure intrinsic semiconductor (such as silicon, germanium, tellurium, etc.). The four electrons of the dopant form bond with Si or Ge and the fifth electron is the 'excess electron' that is loosely bound and can easily be excited from the valence band to the conduction band. Hence, conduction in n-type semiconductor is because of the presence of excess electrons and hence the name n-type (n is used for negatively charged electrons).
- (b) **p-type semiconductor** These are obtained by doping the parent insulator atom with a trivalent impurity such as boron or aluminium (both of them have three valence electrons). The three valence electrons of boron or aluminium form three covalent bonds with three germanium atoms and the fourth germanium atom is linked to boron atom by an incomplete bond containing only one electron from germanium. Thus, the crystal lattice has an electron deficiency called a hole. In the electric field, an electron from an adjacent atom moves into a hole, which is in turn replaced by an electron from another atom. Thus, the condition is brought about because of the migration of holes and hence the name p-type (p is used for positive holes).

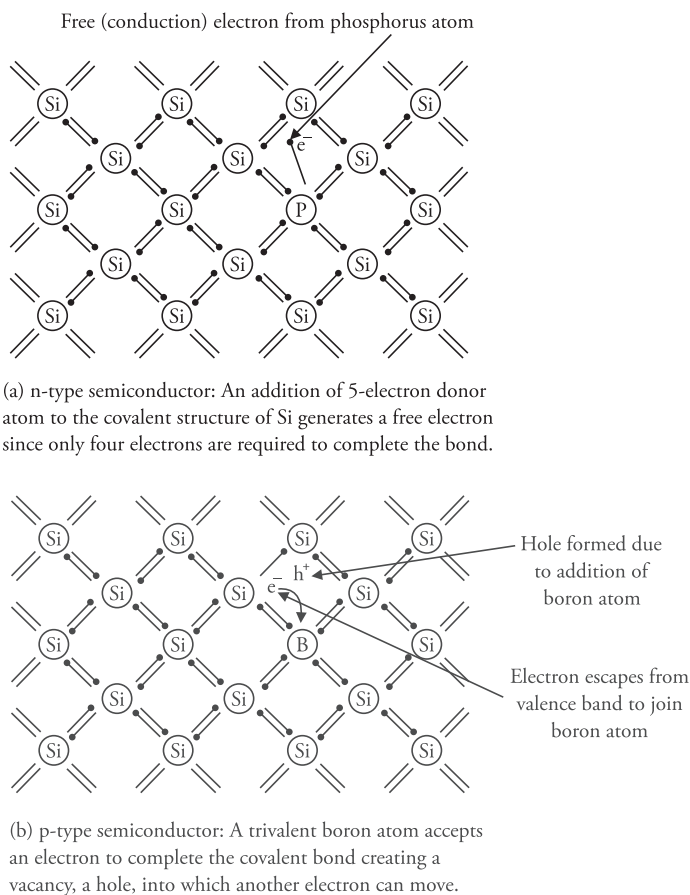


Figure 11.29 Extrinsic semiconductors

Non-Elemental Semiconductors

Silicon and germanium are regarded as elemental semiconductors as they are made up of only type of atoms. Apart from these many semiconductors are made up of more than one type of atoms. These are termed as *non-elemental or inter-metallic or compound semiconductors*. They are formed by the combination of elements of group III and group V as well as from group II and VI. GaAs and GaP are two element (binary) III-V compounds commonly used in light emitting diodes (LEDs) AlSb, InP, InAs, InSb and many metal oxides like ZnO, NiO, FeO and V_2O_5 are other well-known non-elemental semiconductors. Besides these three element (ternary) compounds such as GaAsP and four element (quaternary) compounds such as InGaAsP are also widely used in the electronic industry.

These semiconductors are further classified as: (i) stoichiometric semiconductors and (ii) non-stoichiometric semiconductors

- (i) *Stoichiometric semiconductors* In stoichiometric compounds the number of positive and negative ions is exactly in the ratio as indicated by their chemical formulae. For example the chemical formula of a compound is AB; then it will be a stoichiometric compound if A and B are present in the ratio 1:1. Stoichiometric intermetallic semiconductors are synthesised by the combination of elements of group III and V or group II and VI in the ratio 1:1. GaAs, GaP, InSb, CdTe are well known examples of stoichiometric semiconductors. The crystal structure of these compounds is similar to the crystal structure of pure Si and Ge. Like Si and Ge different elements of these compounds also form four equivalent covalent bonds with four neighboring atoms. These compounds conduct electricity like the elemental intrinsic semiconductors Si and Ge. Like Si and Ge, these intermetallic semiconductors can be doped to get n-type or p-type extrinsic semiconductors. However the forbidden energy gap (E_g) in these semiconductors has wide range (0.25 eV to 2.3 eV) depending upon the nature of the constituent elements. The E_g value in GaAs is 1.35 eV which can be reduced by substituting one of its elements by an element of higher atomic number belonging to the same group. For example, E_g in GaP is 2.24 eV which reduces to 1.35 eV in GaAs (As has higher atomic number than P and both belong to V group). This energy gap is further reduced when As is replaced by Sb (E_g in GaSb is 0.67 eV). The forbidden energy gap (E_g) values of some common intermetallic compounds is given in the following table:

Compound	GaP	GaAs	GaSb	InAs	InSb	CdS	CdSe	PbS	PbTe
Group	III- V	III- V	III- V	III- V	III- V	II-VI	II-VI	II-VI	II-VI
E_g in eV	2.24	1.35	0.67	0.36	0.165	2.42	1.74	0.37	0.25

- (ii) *Non-stoichiometric semiconductors* Non-stoichiometric compounds are those in which the ratio of positive and negative ions present in the compound differs from that required by the ideal chemical formula of the compound. Compound AB would be non-stoichiometric if the ratio of A and B is not exactly 1:1 but contains either excess or deficiency of one type of ions (atomic composition is non-integral $A_{1.1}B$ or $A_{0.94}B$). Oxides and sulphides of transition metal have non-stoichiometric defects in their crystal structure. Such compounds show semiconductivity and are termed as non-stoichiometric semiconductors or defect

semiconductors or hopping semiconductors. Depending upon the type of defect in the lattice structure these semiconductors can be of two types:

(i) n-type (ii) p-type

- (i) *n-type non stoichiometric semiconductor* In n-type semiconductors electrons are the charge carriers. This is observed in non-stoichiometric compounds having either (i) anion vacancies or (ii) extra cations occupying interstitial sites.

Anion vacancy arises when the negative ions are missing from the lattice sites. Absence of anion leaves a vacancy that is occupied by a trapped electron that acts as charge carrier. In the second type an extra cation occupies one interstitial site and an electron is trapped in another interstitial site to maintain electrical neutrality. Zinc oxide is an example of this kind where it loses oxygen reversibly at high temperature. The excess Zn^{2+} ions are trapped in interstitial sites and an equal number of electrons in other sites to maintain electrical neutrality. Under the influence of electric field, these trapped electrons act as charge carriers and hence it is n-type semiconduction. These non-stoichiometric semiconductors containing excess metal ions can be represented as $M_{1+x}Y$. Common examples of these semiconductors are ZnO, CdO, Cr_2O_3 , PbS, ZnS and CdS.

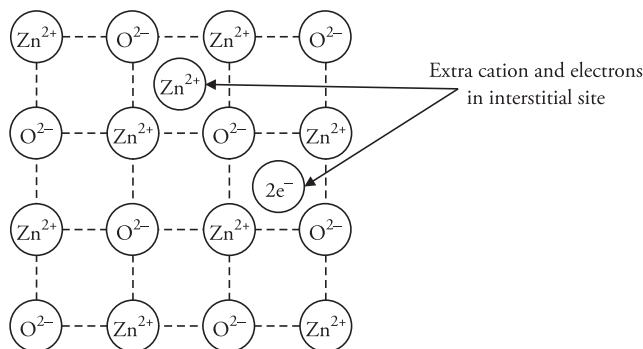


Figure 11.30 Conduction in $\text{Zn}_{(1+x)}\text{O}$ (n-type non-stoichiometric semiconductor)

- (ii) *p-type non-stoichiometric semiconductor* Holes are the major charge carriers in a p-type semiconductor. These compounds are metal deficient and can be represented by the general formula $M_{1-x}Y$. Metals with variable valency (mainly transition metals) form p-type semiconductors. Metal deficiency can arise in two ways:

(i) Cation vacancies (ii) Extra anion occupying interstitial site

- (i) *Cation vacancies* In this case the cation is missing from the lattice site. To maintain electrical neutrality the nearby cation gains an extra positive charge. This type of defect is possible where the metal ion exhibits variable valency like transition metals. Examples are FeO, FeS and NiO.

Let us consider the example of NiO which is made up of Ni^{2+} and O^{2-} ions. If Ni^{2+} ion is missing from the lattice site then two Ni^{2+} ions will acquire Ni^{3+} charge to balance the electrical charges

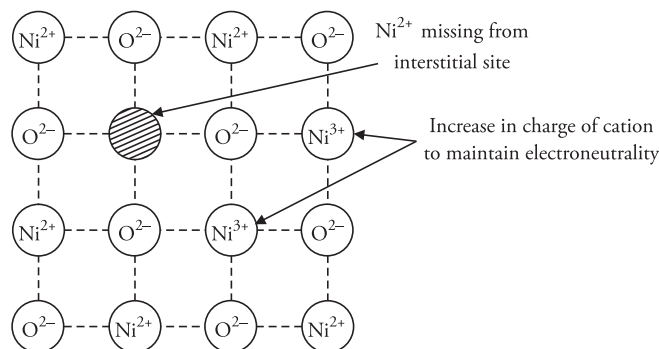


Figure 11.31 Conduction in $\text{Ni}_{(1-x)}\text{O}$ (p-type non-stoichiometric semiconductor)

Since Ni^{3+} is one electron short of Ni^{2+} they may be regarded as holes. If an electron 'hops' from Ni^{2+} to Ni^{3+} then the original Ni^{2+} becomes a new positive centre causing an apparent movement of Ni^{3+} . A series of such 'hopping' movement causes the electron to be transferred in one direction across the structure and at the same time the positive holes migrate in the opposite direction across the structure. Hence these compounds are termed as p-type semiconductors.

- (ii) **Extra anion occupying interstitial sites** In this case, an extra anion occupies the interstitial site. In order to balance the charge, the charge on the adjacent metal increases. Negative ions are usually large; hence, it is difficult for them to occupy the interstitial sites. No crystal containing negative ions in interstitial spaces have been reported so far.

Consequences of metal deficient defects Crystals with metal deficient defects act as semiconductors. The conductivity arises due to movement of electrons from one ion to other. Substances where such types of movements occur are called p-type semiconductors.

- (3) **Controlled valency semiconductors** It is difficult to control the conductivity of non-stoichiometric semiconductors since it depends on the amount of dopants added and the temperature and oxygen pressure employed during its preparation. For example as discussed earlier NiO on oxidation with air produces a p-type semiconductor, $\text{Ni}_{1-x}^{2+}\text{Ni}_x^{3+}\text{O}$ where x varies from 0 to 0.1 with the typical composition $\text{Ni}_{0.7}^{2+}\text{Ni}_{0.2}^{3+}\text{O}$. The conductivity of this semiconductor depends upon the temperature and oxygen pressure employed during its preparation.

The above limitation can be overcome by preparing controlled valency semiconductor. In this type of semiconductor the concentration of Ni^{3+} ions in NiO and hence its conductivity is controlled by adding calculated quantity of lithium oxide (Li_2O).

- (i) **Small Li^+ ion concentration** Doping the host NiO lattice with very small quantity of Li^+ ion reduces the conductivity of p-type semiconductor by decreasing the concentration of Ni^{3+} ions. To maintain electrical neutrality, for every Li^+ ion added the Ni^{3+} changes to Ni^{2+} thereby decreasing the concentration of holes (Ni^{3+}) in the lattice resulting in the decrease in conductivity of p-type semiconductor.

- (ii) *High Li⁺ ion concentration* Doping NiO lattice with moderately high concentration of Li⁺ ions increases the conductivity of p-type semiconductor. In this case the Li⁺ ions substitute the Ni²⁺ ions in their lattice sites. For every Li⁺ ion added a Ni²⁺ ion is converted into Ni³⁺ (hole) to maintain electrical neutrality. Hence the concentration of Ni³⁺ (holes) ions increases in the lattice, thereby enhancing the conductivity of the p-type semiconductor.

For small concentration of Li ions the composition of controlled valency semiconductors of p-type NiO semiconductor at a particular temperature is $Li_x^+ Ni_{1-2x}^{2+} Ni_x^{3+} O$.

Chalcogen semiconductors Elements of group 16 (or VI) in the periodic table are called chalcogens (Greek *chalcos* meaning ‘ore formers’). The chalcogens (sulphur, selenium and tellurium not oxygen and polonium) in conjunction with more electropositive elements like As and Ge and also other elements like Bi, Sb, P, Sn, Pb, B, Al, Ga, In and lanthanides form an important class of materials called *chalcogenides*. These compounds with at least one chalcogen element (S, Se or Te) on melting give viscous liquids which on cooling form glasses called chalcogenide glass. Chalcogenide glasses behave as semiconductors; however, unlike Si and Ge which are crystalline in nature, these are amorphous in nature and behave as p-type semiconductors having unique optical, electrical and photo sensing properties.

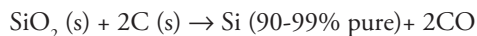
Their electronic conductivity greatly enhances in the presence of light and hence they are also termed as photoconductors or ‘light sensitive semiconductors’. Selenium (or As₂Se₃) is an excellent photoconductor and is employed in xerography or photocopying process.

Preparation of Semiconductors:

The most commonly used semiconductors for electronic devices are Si, Ge and GaAs. However, because of its obvious advantages silicon continues to be the most widely used material in electronic industry. The silicon to be used for semiconducting devices must be at least 99.9999% pure (six nines).

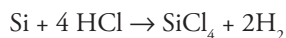
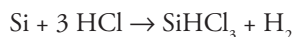
Production of Semiconductor Grade Silicon

Elemental silicon is not available in nature. It is abundantly available in the form of silicon dioxide (sand or quartz) which constitutes nearly 20% of the earth’s crust. Elemental silicon can be obtained from sand (SiO₂) by heating with carbon (metallurgical coke) in an electric arc furnace.

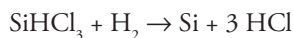


Carbon monoxide combines with atmospheric oxygen to form carbon dioxide which is discharged into the atmosphere and silicon (90%–99% pure) is collected at the bottom of the furnace. The silicon thus obtained is called the *metallurgical grade silicon*.

To obtain semiconductor grade silicon, it is purified further. It is combined with hydrochloric acid to form trichlorosilane SiHCl₃ and small amount of tetrachlorosilane.



SiHCl_3 which is a liquid at room temperature is purified by fractional distillation to remove impurities like iron, copper and also SiCl_4 . SiHCl_3 is reduced by H_2 in a reactor containing high purity silicon rods.



Solid silicon deposits on heated ‘silicon rods’ which grow radially. This process produces rods of semiconductor grade *polycrystalline* silicon.

Zone Refining

Silicon and germanium can be purified by this method. This method is based on the principle that when an impure metal is solidified after melting, crystals of pure metal separate out and the impurities are left behind in the melt. In this method the metal to be purified is cast into a thin rod. One zone of the rod is melted by a circular heater in an inert atmosphere of argon at about 1000 °C. The metal melts at the heated zone. The heater gradually moves from top to bottom and the impurities are swept into the adjacent molten part and are finally discarded (Fig. 11.32). The molten pure metal in the upper region gradually solidifies yielding metal of very high purity.

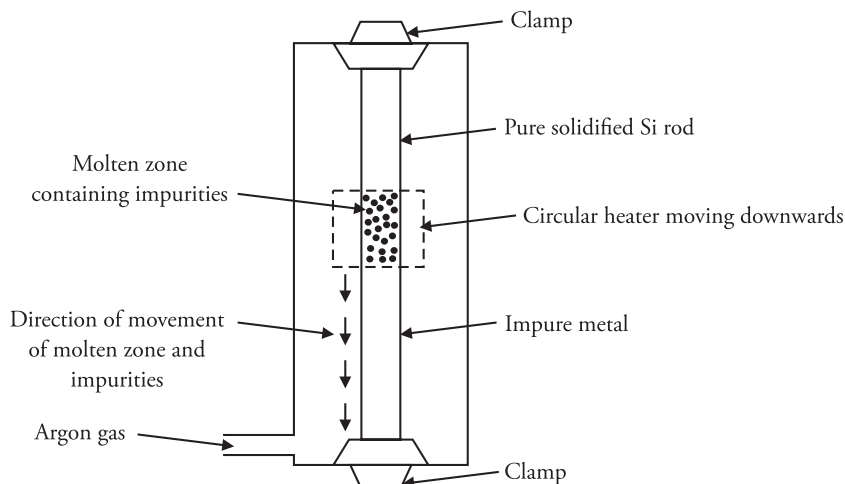


Figure 11.32 Zone refining of silicon.

Single Crystal Formation (Czochralski Process)

Although the purity of silicon obtained by the above two methods is excellent but it is *polycrystalline* composed of many small crystals having random orientation and contains many defects. The silicon used for the fabrication of devices must be nearly perfect and crystalline in nature. *Crystal growth*

method is used to produce single crystals of silicon. This method converts a randomly oriented or polycrystalline material into an orderly and crystalline material.

The easiest method to achieve this is to melt silicon and let it freeze. *Czochralski process* is commonly used for the single crystal formation. A Czochralski (CZ) apparatus consists of a crucible, heating element, power supply, seed shaft, rotating mechanisms and vacuum systems all of which are controlled by microprocessors and sensors. The experimental setup is shown in Figure 11.33. A typical CZ apparatus weighs about 20 tonnes, is 7 to 8 metres tall and can hold a charge of 100 kg of silicon. The semiconductor grade polycrystalline silicon is melted in a quartz lined graphite crucible. The melt is maintained at a temperature of 1690 K, which is slightly greater than the melting point of silicon (1685 K). The temperature is controlled carefully by surrounding heaters and heat shields in such a way that the center of the melt is the coolest.

A single silicon crystal of desired orientation is attached on the rod to act as the seed crystal and it is made to touch the surface of the melt. The rod is rotated in the molten material and the crystal is pulled out of the melt. The molten semiconductor solidifies on the seed crystal with an identical structure and orientation.

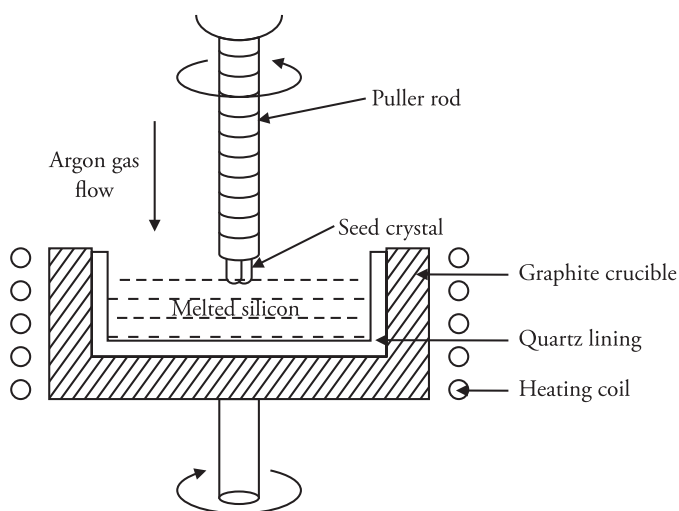


Figure 11.33 Czochralski method of single crystal growth

Wafer Manufacture

The diameter of the obtained crystals is nearly 20–30 cm. These crystals are removed and ground to be perfectly round and then they are cut into thin discs called *wafers*.

Doping Techniques

Calculated quantity of dopant (B, P, As or Sb) is added to the melt before the crystal pulling stage. The commonly employed doping techniques are as follows:

- (a) *Diffusion* In this process the dopants are introduced into the wafers by *solid state diffusion*. In the first step the vapours of the dopant atoms are deposited at the silicon surface at a high temperature of 1000 °C. At this temperature the silicon atoms move out of their lattice sites creating high density of vacancies. The dopant atoms on the surface move into the vacant locations of the silicon atom.
- (b) *Ion implantation* This process is employed for doping at lower temperature. In this the dopant can be introduced into selected areas of the wafer. The semiconductor material is bombarded with an electrically controlled beam of high energy ions of B or P with energy of the order of 10,000 eV. This causes the implantation of the dopant into the crystal lattice of the semiconductor.
- (c) *Epitaxy* It is the process of deposition of a thin crystal layer on a crystalline *doped* layer of the substrate. The lattice spacing and the structure of the material in epitaxial layer must be close to that of the substrate, for example, Si on Ge or Ge on Si or Si–Ge solid solution grown on Si. The substrate and grown crystal usually differ in the level and type of doping.

Chemical vapour deposition (CVD) process is commonly employed for epitaxial growth. Silicon wafers are placed in a boat shaped crucible made up of graphite. The boat is placed in a cylindrical quartz tube reactor which is heated by induction using heating coils wound around the tube. The gases containing compounds of Ge or Si mixed with calculated quantities of the dopant are introduced into the reactor. The epitaxial layer is grown from the vapor phase onto silicon which is in solid state. The doped wafer thus obtained is ready for fabrication.

A silicon epitaxial film is obtained using a mixture of SiCl_4 , H_2 and N_2 . This mixture is mixed with calculated amount of phosphine (PH_3) for n-type and with diborane (B_2H_6) for p-type doping.

Semiconductor Devices

A large number of semiconductor devices such as rectifiers, transistors, photocells and solar batteries are known. All these devices use intrinsic and extrinsic semiconductor crystals.

If a part of a block of silicon crystal is doped with pentavalent impurity it has n-type characteristics and the other part doped with a trivalent impurity will have p-type characteristics. The boundary between the two regions of opposite characteristics is called the *p-n* junction. This block of silicon with n-type, p-type portion and a *p-n* junction constitutes a basic diode which conducts current only in one direction. This property of a *p-n* junction has many applications in electronic industry.

- (i) *p-n junction diode as a rectifier* A *p-n* junction diode is an electronic device that helps the current to flow in one direction only. It is used to transform an alternating current into direct current.

If the negative terminal of the battery is connected to n-type semiconductor and positive terminal of the battery is connected to p-type semiconductor (Fig. 11.34 b) it is referred to as forward bias and if the negative terminal of the battery is connected to p-type semiconductor and positive terminal to n-type it is termed as reverse bias.

In forward bias the negative terminal of the battery repels the electrons in the conduction band of n-type semiconductor and they are attracted towards the positive terminal. Similarly

the positive terminal of the battery repels the holes in the conduction band of p-type semiconductor which are attracted towards the negative terminal. The electrons and holes encounter each other near the junction where they combine with each other. Hence in forward bias, as long as the device is connected to the battery there is flow of current across the semiconductor and to the junction.

If the connection are reversed as in reverse junction (Fig. 11.34 c) the charge carriers move in the reverse direction. The electrons of n-type semiconductor are attracted towards the positive terminal of the battery and the holes of p-type semiconductor are attracted towards the negative terminal of the battery. Consequently the charge carriers move away from the p - n junction. Hence if a p - n junction is a part of a circuit subjected to alternating current it acts as a rectifier allowing current to flow in half of the cycle (forward bias) and inhibiting the current flow during another half of the cycle (reverse bias). Hence the current flows in one direction only.

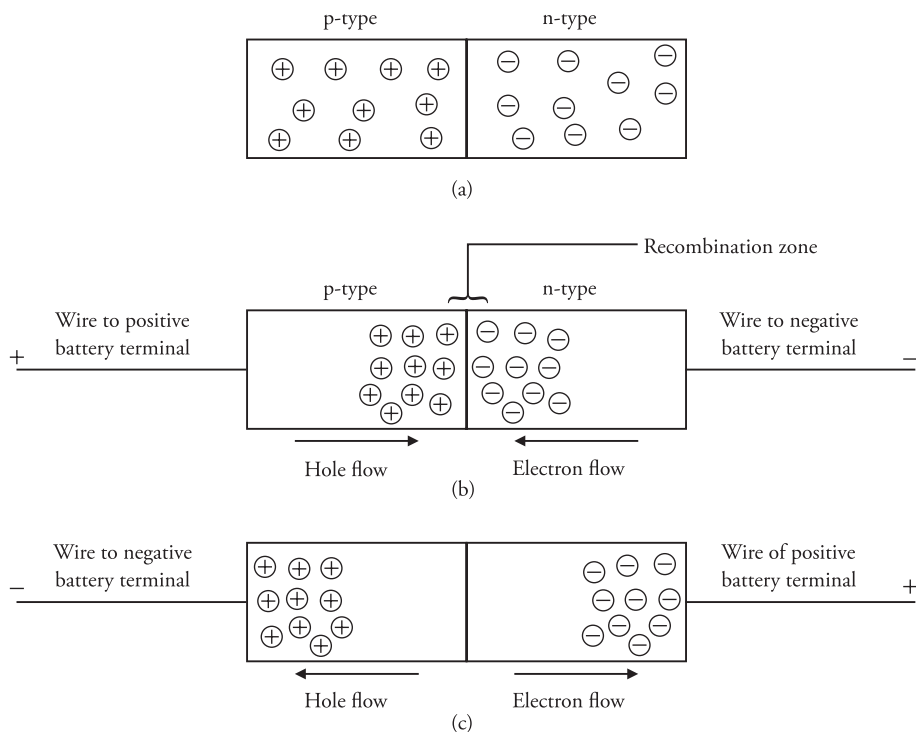


Figure 11.34 A semiconductor diode rectifying junction showing distribution of electrons: (a) When there is no electrical potential, (b) forward bias and (c) reverse bias

It is important to note that the rectified output of this circuit is only half of the input ac wave hence it is called a half wave rectifier (Fig. 11.35). Use of two diodes gives output rectified voltage for both positive and negative half of the ac cycle and hence it is known as full wave rectifier.

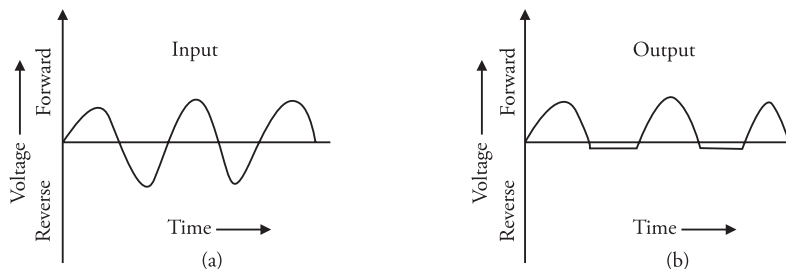


Figure 11.35 (a) Alternating current input in a semiconductor diode.
(b) Direct current output after rectification (half wave rectification)

(ii) *Junction transistor* Transistors are very important electronic devices which are used to amplify an electric signal. A transistor consists of two $p-n$ junctions in the same crystal arranged in either the $n-p-n$ or the $p-n-p$ configuration. In the $n-p-n$ transistor a very thin p -region acting as the *base* is sandwiched between the two n -regions (Fig. 11.36). One of the n -region acts as the emitter and the other acts as the collector. All the three segments of a transistor have different thickness and doping levels hence the emitter and collector are not interchangeable. A brief description of the three segments is given below:

- *Emitter* The emitter is of moderate size and is heavily doped. It supplies large number of majority carriers (electrons in $n-p-n$ transistor and holes in $p-n-p$ transistor) for current flow through the transistor.
- *Base* It is the central segment of the transistor; it is lightly doped and is kept as thin as possible.
- *Collector* As compared to the emitter, the collector is moderately doped and larger in size. It collects a major portion of the majority carriers supplied by the emitter.

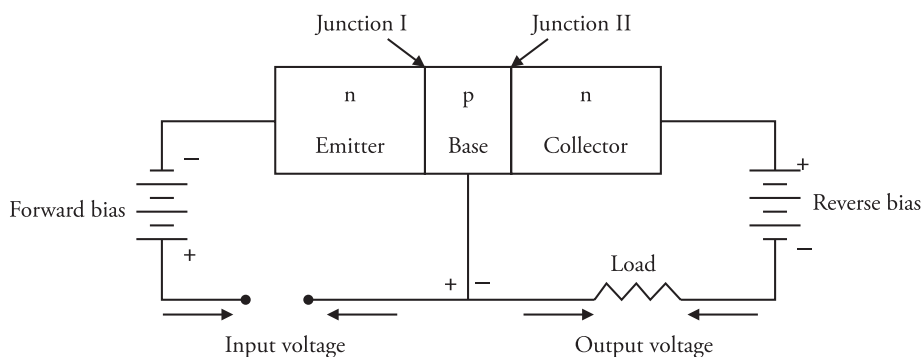


Figure 11.36 Schematic diagram of $n-p-n$ junction transistor associated with its circuit

The emitter–base junction (junction 1) is forward biased and the collector–base junction (junction 2) is reverse biased. A transistor biased in this way is said to be in an *active state*. The emitter base junction is connected to the input signal and the collector base junction is connected to the output signal as shown in Figure 11.36. On applying voltage the majority carriers (electrons in n - p - n transistor) enter the base region in large numbers. These electrons can recombine with the holes in the base region but since the base region is very thin and lightly doped all the majority carriers are swept through the base without recombination and cross junction 2 (base–collector junction) and enter the collector. In an ideal transistor almost all the electrons emitted reach the collector by flowing through the base and down the potential hill of the base collector junction. From the above description it is clear that in active state of the transistor the emitter–base junction acts as a low resistance while the base–collector junction acts as a high resistance. A small change in input voltage results in a large current from the emitter to the base and then on to the collector. The current flowing through different regions being the same, this large current can appear as a large voltage across the load resistor, if its resistance is high. Thus amplification results (Fig. 11.37).

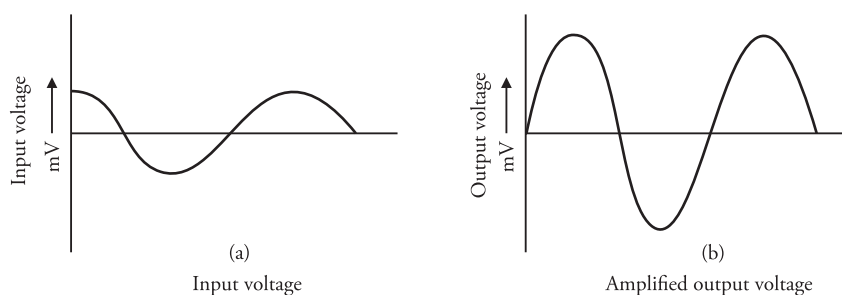


Figure 11.37 Input and output voltage characteristics of a transistor showing voltage amplification

Functioning of p - n - p transistor is similar to the n - p - n transistor, except that holes are injected from emitter to the base and these holes then cross the base into the collector region.

11.15 Superconductors

In 1911, a Dutch physicist, Kamerlingh Onnes at the University of Lieden in Holland, observed that when a sample of mercury is cooled with liquid helium to 4.2 K its electrical resistance vanishes completely and it becomes superconducting. He termed this phenomenon as superconductivity and the temperature below which an element exhibits superconductivity was termed as the critical temperature or the superconducting transition temperature T_c . Further studies showed that materials in superconducting state are repelled by magnets, that is, they become perfect diamagnets. Moreover if a superconducting material is placed in a magnetic field above its T_c , the magnetic lines of force will penetrate the sample; however, when this material is cooled below T_c it not only repels the magnetic flux but excludes all magnetic flux from its interior. This phenomenon is termed *Meissner effect*.

Properties of Superconductors:

1. They exhibit zero resistivity below T_c and at room temperature they possess greater resistivity than normal metals (Fig. 11.38).
2. X-Ray diffraction studies reveal that there is no change in the crystal structure due to this transition. This shows that electrons and not atoms conduct electricity in superconductors.
3. The thermal expansion and elastic properties do not change in transition.
4. Superconductors are perfect diamagnets and below T_c they expel all magnetic flux from their interior (Meissner effect; Fig. 11.39).
5. The critical temperature can be lowered by the addition of impurities to a superconducting material.
6. All thermoelectric effects disappear in superconductivity state hence there are no heating losses.
7. When a very strong magnetic field is applied to a superconductor below critical temperature its superconducting property is destroyed.

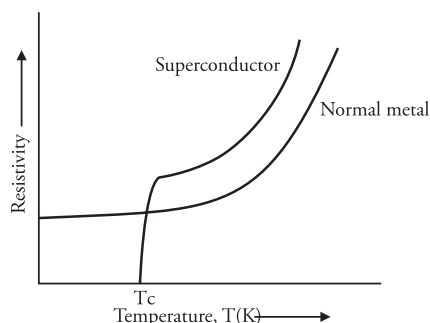


Figure 11.38 Resistivity variation of a normal metal and superconducting metal with temperature

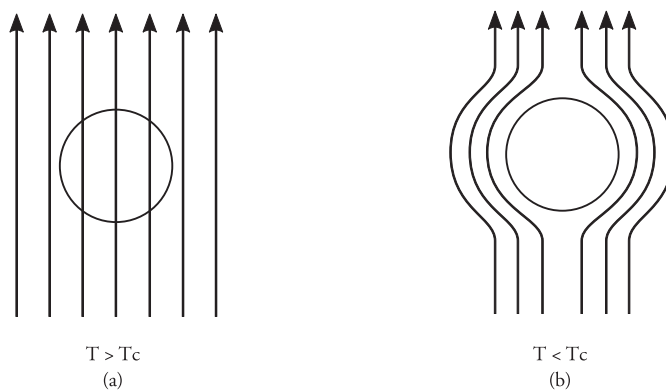


Figure 11.39 Meissner effect: A superconductor expels all magnetic flux from its interior below its critical temperature

Type I and Type II Superconductors

It has been observed that below the critical temperature the superconductivity of a material disappears if it is placed in a magnetic field exceeding a critical value B_c . The critical value of magnetic field depends on temperature and is characteristic of the material. A superconducting material below T_c will continue to be a superconductor as long as the applied magnetic field is below B_c and will revert to normal state when the field exceeds B_c (Fig. 11.40).

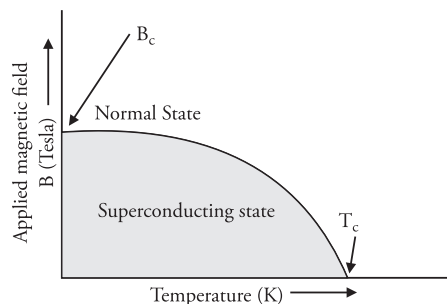


Figure 11.40 Superconducting metal below T_c returns to normal state if applied field is greater than B_c

On the basis of their diamagnetic properties superconductors are classified into two types called type I and type II. In type I superconductors, as the applied magnetic field B increases, so does the opposing magnetisation M until the field reaches the critical field B_c , where upon the superconductivity disappears. At this point, the perfect diamagnetic behaviour, the Meissner effect is lost (Fig. 11.37 a). In other words, a type I superconductors exhibits Meissner effect below B_c and expels all magnetic flux from its interior but above B_c it is in the normal state where magnetic flux penetrates the sample and conductivity is finite.

In type II superconductors the transition from Meissner state to normal state does not occur sharply but it goes through an intermediate state in which the applied field is able to penetrate certain regions of the superconducting material. As the magnetic field increases initially the metal expels all magnetic flux from its interior and behaves as a perfect diamagnet (exhibit Meissner effect). When the applied field increases beyond critical magnetic field B_c , the magnetic flux is not totally expelled from the material. Although the overall magnetisation M opposes the field but it does not cancel the field completely. This is termed as the lower critical field B_{c1} . As the applied field increases M gets smaller and smaller and more and more flux lines penetrate the sample till the upper critical field B_{c2} is reached wherein all the flux lines penetrate the sample and the material returns to the normal state and its superconductivity disappears. The state between B_{c1} and B_{c2} is called the mixed state or vortex state.

All engineering applications invariably use type II materials because of their higher critical temperature and higher critical magnetic field.

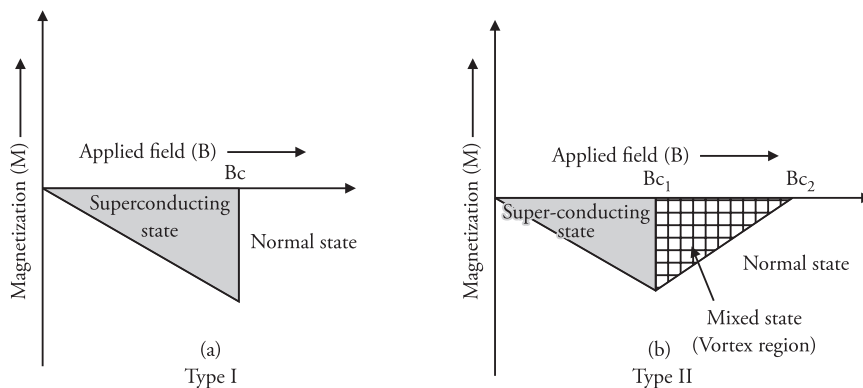


Figure 11.41 (a) Type I superconductor. Magnetic field inside the sample is zero when $B < B_c$; (b) Type II superconductor. Magnetic field inside the sample is zero when $B < B_{c1}$

High temperature superconductors

Until 1986 the highest known value of T_c was 23.2 K for the compound Nb_3Ge . In 1986 K Alex Muller and J. Georg Bednorz reported a nonstoichiometric barium lanthanum copper oxide $Ba_xLa_{2-x}CuO_4$ (here x has a value of about 0.1), a ceramic material with a T_c value of 35 K. Later compounds with still higher T_c values were discovered. $YBa_2Cu_3O_{7-x}$ (where $x < \text{or equal to } 0.5$) has T_c value of about 90 K. This compound is called 1-2-3 compound (ratio Y: Ba: Cu is 1:2:3). This compound can be prepared by heating powdered mixture of Y_2O_3 , $BaCO_3$ and CuO in right proportion to temperature between 900 and 1100 °C for about 10-12 hours. The product is then annealed at 800 °C in an atmosphere of oxygen so that the mixture absorbs requisite amount of oxygen. It is further cooled in air to obtain the sample having composition $YBa_2Cu_3O_{7-x}$.

Structure of high temperature superconductors The structure of the powder product obtained is akin to that of ABO_3 cubic structure of mineral perovskite ($CaTiO_3$). Three body centered cubic unit cells are stacked one above the other (Fig. 11.42). The distribution of atoms in the unit cells is as follows:

Cu at the corners $8 \times 1/8 \times 3 = 3$

Ba at the two body centres $1 \times 2 = 2$

Y at the one body centre $1 \times 1 = 1$

O at mid-point of edges $12 \times 1/4 \times 3 = 9$

Some oxygen positions are vacant and their number varies from 6.5 to 7.

Applications of superconductors:

The phenomenon of superconductivity has many applications some of which are discussed below:

1. As there are no I^2R losses in superconductor, power can be transmitted to long distances through superconducting cables without loss.

2. Application of Meissner effect includes high speed magnetically levitated trains used in transportation.
3. Powerful superconducting magnets are used in magnetic resonance imaging (MRI) instruments used in medical diagnosis.
4. Superconductors are used to make magnets for high energy particle accelerators.
5. Superconducting materials help in the manufacture of exceptionally small transformers and generators with efficiency 99.99%.
6. Superconductors are also used in the manufacture of high speed switching and signal transmission for computers.

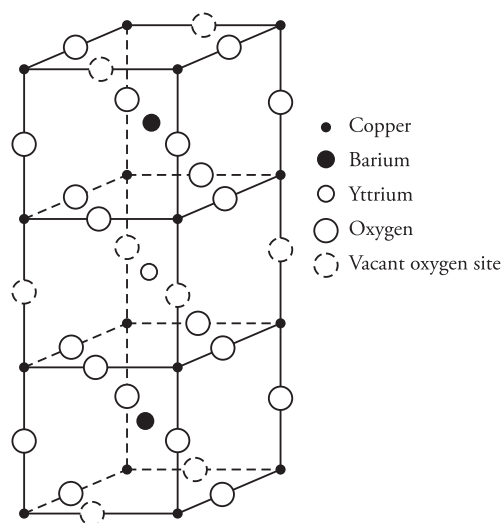


Figure 11.42 The crystal structure of yttrium-barium-copper oxide

Insulators

As discussed in the previous sections insulators are materials which resist the flow of electricity through them. In terms of the band theory there is a large energy gap (5–10 eV) between the valence band and conduction band. As a result the valence electrons are unable to migrate into the conduction band, hence they do not conduct electric current under the influence of electric field. The situation discussed above is an ideal situation but practically a perfect insulator does not exist. Even insulators have small numbers of charge carriers which enable them to carry current. Moreover when a sufficiently high voltage is applied across an insulator the electrons become free from the atom and the insulator becomes electrically conducting. The voltage at which the above change occurs is termed as the *breakdown voltage*.

Insulators are also known as *dielectrics*. The ability of an insulator to resist puncture or rupture due to electric field intensity is known as the *dielectric strength* which is commonly expressed in volts per mm thickness of the material. Insulators/dielectric materials find extensive use in electrical industry for insulation purposes and as capacitors. They can be of different types depending on the use to which they are put. A detailed discussion of insulating materials is given in Section 5.8.

11.16 Magnetic Materials

The magnetic properties of materials are used in many engineering devices such as transformers, inductors, ferrite antennas and rotating machines. Most of the engineering devices utilise the ferromagnetic and ferrimagnetic properties of materials which are therefore more important as compared to diamagnetism and paramagnetism.

Classification of magnetic materials

Magnetic materials are classified into five groups:

- (1) Diamagnetic
- (2) Paramagnetic
- (3) Ferromagnetic
- (4) Antiferromagnetic
- (5) Ferrimagnetic

Diamagnetism It is non-permanent and weak form of magnetism that persists as long as an external field is being applied. The orbital motion of charge carrying electrons in an atom is analogous to current carrying coil. When an external magnetic field is applied to an atom the orbital motion of the electrons is modified in such a way that a weak magnetic moment opposing the field is induced. The magnetic susceptibility is negative, that is, the magnitude of the field B within a diamagnetic solid is less than that in vacuum. When a diamagnetic material is placed in a magnetic field it repels the magnetic lines of force (Fig. 11.43a), for example, copper, silver, gold, bismuth and superconductors below critical temperature.

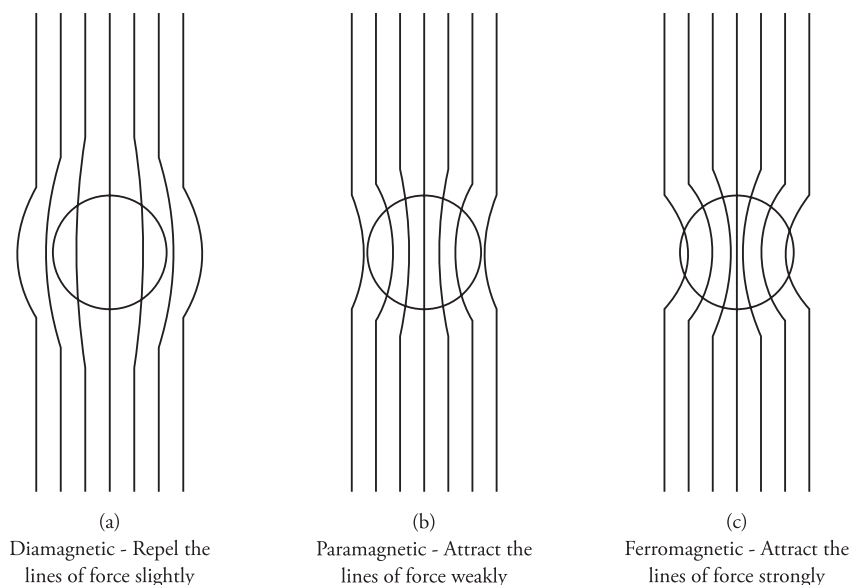


Figure 11.43 *Diamagnetism, paramagnetism and ferromagnetism*

Paramagnetism Paramagnetic materials have a small positive magnetic susceptibility. When a magnetic field is applied to a paramagnetic material the magnetic flux density increases slightly. These materials attract the magnetic lines of force, the degree of magnetisation being proportional to the strength of the field, for example, alkali and transition metals like aluminium, chromium, molybdenum, sodium, titanium and zirconium.

Ferromagnetism The magnetic susceptibility for ferromagnetic material is large and positive. They are strongly attracted by the magnetic field and retain magnetism even after the magnetising field is removed, that is, they can be permanent magnets, for example, iron, cobalt and nickel.

Antiferromagnetism In some materials like MnO the magnetic moments are aligned in such a way that the magnetic moments of adjacent ions are anti parallel so that they cancel each other. Consequently the solid as a whole possesses no net magnetic moment.

Ferrimagnetism Some ceramics exhibit a permanent magnetisation termed as ferrimagnetism. Ferrimagnetism is explained on the basis of magnetic ordering. The magnetic moments of the constituent atoms are aligned in parallel and antiparallel direction in unequal numbers. The oppositely directed magnetic moments have different magnitudes and do not cancel each other completely. Hence, the crystal possesses magnetisation even in the absence of an applied magnetic field. Examples include Fe_3O_4 and MFe_2O_4 , where M represents any one of the several metal atoms.

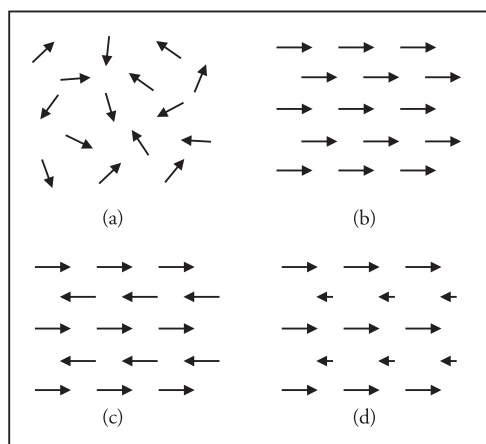


Figure 11.44 Four kinds of magnetism with various interatomic interaction. (a) Paramagnetism, (b) ferromagnetism, (c) antiferromagnetism and (d) ferrimagnetism

It is important to note that all magnetically ordered solids (ferromagnetic, antiferromagnetic and ferrimagnetic) transform into paramagnetic state at high temperature due to the randomisation of their spins.

11.17 Fullerenes

Until 1985, carbon was known to exist in two allotropic forms, diamond and graphite. In 1985, Robert Curl, H.W. Kroto and R. Smalley at Rice University, USA, discovered the third allotrope of carbon – C_{60} . The molecule has a truncated icosahedron structure. The 60 carbon atoms are

arranged in pentagons and hexagons. A molecule of fullerene is found to consist of 20 hexagons and 12 pentagons, which are arranged in such a way that no two pentagons share a common side. The molecule resembles a football or soccer ball (Fig. 11.45). Fullerene is popularly known as buckminsterfullerene to honour the American architect Buckminster Fuller who designed geodesic domes based on hexagons and pentagons. The shape of C_{60} resembles that of such domes designed by Fuller.

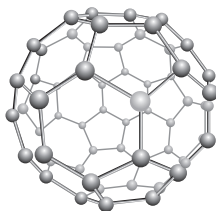


Figure 11.45 Structure of fullerene

Types of fullerenes

Fullerenes can be of various types

- (i) *Spherical fullerenes* These are known as bucky balls, for example, C_{60} (discussed above)
- (ii) *Cylindrical fullerenes* These are called *carbon nanotubes* or *bucky tubes*. They are very strong, have a very high tensile strength, high electrical conductivity, high ductility and high heat conductivity (explained in Chapter 23, Nanochemistry).
- (iii) *Planar fullerenes* They are in the form of sheets, for example, graphene. (discussed in Chapter 23, Nanochemistry)

Other fullerenes

C_{60} was the first discovered fullerene. Now C_{24} , C_{28} , C_{32} , C_{36} , C_{50} , C_{70} , etc., have also been isolated. C_{20} is the fullerene containing the least number of carbon atoms. It has been prepared synthetically.

Preparation of fullerenes

- (i) *Arc vaporisation of graphite* Fullerene was prepared in 1990 by physicist W. Kratschmer and D.R. Huffman by simple resistive vaporisation of graphite in an atmosphere of helium. Resistive vaporisation is initiated by passing high current through the rods. The black soot contains C_{60} and larger fullerenes, which can be extracted using various chromatographic techniques.
- (ii) *Contact arc method* In this method, arc vaporisation was modified by maintaining an electric arc between the two graphite electrodes in contact with an atmosphere of helium. Most of the power is dissipated in the arc. Individual fullerenes can be separated by chromatographic technique using alumina–hexane.
- (iii) *Other methods* By combustion of hydrocarbons, up to 40% fullerene containing soot can be prepared from a benzene–oxygen combustion flame in an atmosphere of argon.

Properties of C_{60}

- (i) It is a black powdery material.
- (ii) It gives a magenta coloured solution in aromatic hydrocarbons.
- (iii) Unlike the other two allotropes of carbon, C_{60} exists as a discrete molecule.
- (iv) It forms a translucent magenta face-centred cubic crystal on sublimation.

- (v) It reacts with alkali metals to form fullerides of type M_3C_{60} . These fullerides are reported to exhibit superconductivity at low temperatures.

Applications

1. When mixed with alkali metals, they can be used to produce superconductors.
2. It serves as a lubricant due to its spherical structure. The bucky ball acts as molecular ball bearing.
3. Used to prepare soft ferromagnets with zero remanence (TDAE C_{60}) (tetrakisdimethylamino ethylene).
4. They can also be used in rechargeable batteries as catalysts, in microelectronic devices, non-linear optical devices, etc.

11.18 Graphite

Graphite is the second allotrope of carbon. It has a large structure. The carbon atoms are arranged in the form of a hexagon (Fig. 11.46). The carbon atoms in the hexagon are sp^2 hybridised. Only three valence electrons of each carbon atom are involved in forming σ bonds (using sp^2 hybrid orbital). The fourth electron forms a π bond. The π electrons are mobile, delocalised and responsible for the electrical conductivity of graphite.

The layers of graphite are loosely bonded by weak van der Waals forces. Because of these weak bonds between different layers, they slip over each other making graphite soft and slippery.

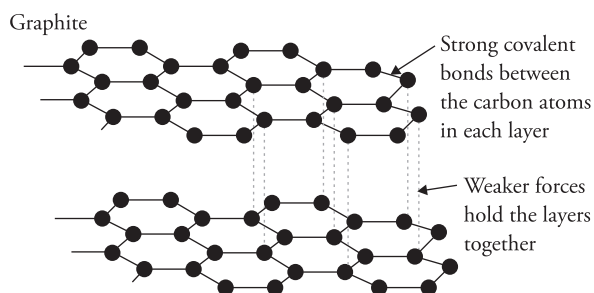


Figure 11.46 Structure of graphite

Uses

1. It is used in pencils for writing. In fact, graphite owes its origin to the Greek word '*graphein*', which means 'to draw or write'.
2. It is used as a lubricant in brake linings.
3. Because of the high melting point, it is used in making crucibles, refractories and moulds containing molten metals.
4. It is used for making carbon brushes in electrical motors.
5. High purity graphite is used for producing moderator rods for reactors.

Summary

- Solids are substances with definite shape and volume.
- Solids can be crystalline with long range order and amorphous with short range order.
- Based on the nature of intermolecular forces, solids are of four types – molecular solids, ionic solids, covalent solids and metallic solids.
- The smallest unit which on repeating itself indefinitely forms a crystal lattice is called the unit cell. Unit cells when repeated over and over again produce the complete space lattice.
- There are 14 Bravais lattices derived from seven crystal forms.
- Three types of unit cells are known – simple cubic, body centred cubic and face centred cubic.
- The number of atoms per unit cell are 1 for a simple cubic, 2 for a body centred cubic and 4 for a face centred cubic.
- The number of atoms touching a given sphere is called its coordination number. The coordination number in a simple cubic arrangement is 6 and in a body centred cubic is 8; the hexagonal close packed and cubic close packed arrangement have a coordination number of 12.
- The geometry and coordination number of a crystal depends on the radius ratio, which is the ratio of the radius of a cation to the radius of an anion.
- Bragg's law – When X-ray is incident on a crystal, it is diffracted from the atoms in the crystal planes and obeys the laws of reflection. If the angle of incidence is θ , then the angle of reflection will also be θ . Constructive interference will occur if the path difference between the two rays reflected from successive planes is an integral multiple of their wavelengths. According to Bragg $n\lambda = 2d \sin \theta$.
- When the atoms or electrons in a crystal do not occupy their lattice sites, the crystal is said to have a defect or an imperfection.
- The imperfection due to electrons is termed electronic imperfections and those due to atoms are called point defects or atomic imperfections.
- A Schottky defect is a point defect in which an ion is missing from the lattice site.
- A Frenkel defect is a point defect in which an ion leaves the lattice point and occupies the interstitial space.
- Crystal defects alter properties like conductivity, colour, etc.
- Semiconductors are of two types:
 - (i) Elemental semiconductors
 - (ii) Non-elemental semiconductors
- Elemental semiconductors are made up of only one type of atoms and may be intrinsic semiconductors or extrinsic semiconductors.
- Extrinsic semiconductor in which charge carriers are electrons are called n-type semiconductors and those in which charge carriers are holes are called p-type semiconductors.

- Non-elemental semiconductors are made up of more than one type of atoms. They are also termed as intermetallic or compound semiconductors.
- Non-elemental semiconductors can be stoichiometric semiconductors and non stoichiometric semiconductors.
- Chalcogen semiconductors are semiconductors containing elements of group 16 or VI. They are light sensitive and are called photoconductors.
- Elemental silicon is obtained from silica by heating with carbon in an electric arc furnace or by zone refining.
- Semiconductor grade silicon is obtained by the Czochralski process.
- Silicon can be doped by various techniques like diffusion, ion implantation and epitaxy.
- A $p-n$ junction diode is used as a rectifier and a $p-n-p$ or $n-p-n$ junction is used in transistors for amplification.
- Superconductors are substances that have zero resistivity.
- Magnetic materials are placed in five categories – diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic.
- Most of the engineering devices utilise the ferromagnetic and ferrimagnetic properties of materials.

Review Questions

1. What is solid state chemistry? Classify solids on the basis of the molecular forces. Differentiate between crystalline solids and amorphous solids.
2. Define: (i) Crystal lattice (ii) Unit cell
3. Explain the various types of Bravais lattices with the help of suitable examples.
4. What are the different types of unit cells? How many atoms per unit cell are present in each of them?
5. Define coordination number in crystals. Discuss the following type of cubic structures:
 - (i) Simple cubic
 - (ii) Body centred cubic
 - (iii) Face centred cubic
6. What is radius ratio? How is it related to the coordination number and structure of the crystal?
7. What are interstitial voids? Explain the different types of voids present in a crystal structure.
8. Prove that the packing efficiency of a face centred cubic arrangement is 74 per cent.
9. Derive Bragg's equation for diffraction of X-rays by crystals.
10. Derive an expression for the density of a cubic crystal.

11. Explain the structures of the following ionic compounds:
 - (i) NaCl
 - (ii) ZnS
 - (iii) CsCl
 - (iv) CaF_2
 - (v) Na_2O
12. What are imperfections in solids? Explain electronic and atomic imperfections in detail.
13. What are stoichiometric crystals? Explain the various defects in stoichiometric crystals.
14. What are non-stoichiometric crystals? Discuss the different types of defects in them.
15. Write down the preparation, properties and uses of fullerene and graphite.
16. What are elemental semiconductors? With the help of silicon semiconductors explain the phenomenon of conduction in intrinsic and extrinsic semiconductors.
17. What are non-elemental semiconductors? Why are they termed as compound semiconductors? Explain the conduction phenomenon in stoichiometric and non-stoichiometric semiconductors.
18. It is difficult to control the conductivity of non-stoichiometric semiconductors. Explain how this limitation can be overcome by the use of controlled valency semiconductors.
19. What are chalcogen semiconductors? Explain their application as light sensitive semiconductors.
20. Explain the phenomenon to obtain semiconductor grade silicon from silica.
21. With the help of a well labeled diagram explain the Czochralski process of obtaining crystalline silicon.
22. Write short notes on:
 - (a) Doping techniques
 - (b) p - n junction diode as a rectifier
 - (c) p - n junction diode as a transistor
 - (d) Meissner effect
23. What is a superconductor? Explain the difference between type I and type II superconductors.
24. What are high temperature superconductors? Describe the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.
25. What are magnetic materials? Classify the various magnetic materials.

Multiple Choice Questions

1. Amorphous solids
 - (a) Have sharp melting points
 - (b) Undergo sharp cleavage when cut with knife
 - (c) Do not undergo sharp cleavage when cut with knife
 - (d) Possess orderly arrangement over long distances.
2. Graphite is an example of
 - (a) Ionic crystal
 - (b) Covalent crystal
 - (c) Metallic crystal
 - (d) Molecular crystal

3. Crystals can be classified into
 - (a) 7 crystal systems
 - (b) 4 crystal systems
 - (c) 3 crystal systems
 - (d) 14 crystal systems
4. An atom in the face centered cubic cell is shared by
 - (a) 2 unit cells
 - (b) 4 unit cells
 - (c) 6 unit cells
 - (d) 1 unit cell
5. The number of atoms per unit cell in a body centered crystal are
 - (a) Four
 - (b) One
 - (c) Two
 - (d) Three
6. In a FCC arrangement the number of nearest neighbour for a given lattice point is
 - (a) 14
 - (b) 12
 - (c) 6
 - (d) 8
7. 8:8 type of packing is present in
 - (a) CsCl
 - (b) KCl
 - (c) NaCl
 - (d) MgCl_2
8. Braggs law is given by
 - (a) $n\lambda = 2d \sin \theta$
 - (b) $n\lambda = d \sin \theta$
 - (c) $2n\lambda = d \sin \theta$
 - (d) $n \frac{\theta}{2} = \frac{d}{2} \sin \lambda$
9. An element A crystallises in ccp arrangement. B occupies half of the tetrahedral sites. The empirical formula of the compound is
 - (a) AB
 - (b) AB_2
 - (c) A_2B
 - (d) A_2B_3
10. When an ion occupies the interstitial site in the crystal lattice, the defect is known as
 - (a) Schottky defect
 - (b) Frenkel defect
 - (c) Crystal defect
 - (d) Point defect
11. An ion is lost from the crystal lattice and to maintain electrical neutrality another ion is lost from another position. Such defects are known as
 - (a) Interstitial defect
 - (b) F-centres
 - (c) Schottky defects
 - (d) Frenkel defect
12. The unit cell with crystallographic dimension $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$ is
 - (a) Cubic
 - (b) Tetragonal
 - (c) Tetrahedral
 - (d) Rhombohedral
13. The radius ratio for an octahedral arrangement is
 - (a) 0.155 – 0.225
 - (b) 0.225 – 0.414
 - (c) 0.414 – 0.732
 - (d) 0.732 – 1.0

14. A binary solid A^+B^- has a rock salt structure, if the edge length is 400 pm and the radius of cation is 75 pm the radius of anion is
(a) 100 pm (b) 125 pm
(c) 325 pm (d) 250 pm
15. The solid X^+Y^- has a BCC structure. If the distance of closest approach between the two atoms is 1.73 \AA , the edge length of the cell is
(a) $\sqrt{2}$ pm (b) $\sqrt{3/2}$ pm
(c) 100 pm (d) 142.2 pm
16. When a crystal loses an anion it results in a metal excess defect. To maintain electro neutrality an electron is trapped at the anion site. These vacant sites occupied by trapped electrons are termed as
(a) F centres (b) A centres
(c) G centres (d) X centres
17. The fullerene first discovered by Buckminster is
(a) C_{24} (b) C_{32}
(c) C_{48} (d) C_{60}
18. Which of the following is not a molecular solid
(a) Solid carbondioxide (b) Ice
(c) Quartz (d) Iodine
19. Pure silicon at 0 K is an
(a) Intrinsic semiconductor (b) Extrinsic semiconductor
(c) Insulator (d) Conductor
20. The majority charge carriers in p-type semiconductor germanium are
(a) Free electrons (b) Ions
(c) Electrons in the conduction band (d) Holes
21. Metallurgical and semiconductor grade silicon have the purity of about
(a) 99% and 99.9999% respectively
(b) 99.99% and 99% respectively
(c) 98% and 99.999% respectively
(d) 99.99% and 99.999% respectively
22. During purification of Si, the liquid that is produced by dissolving Si in HCl is
(a) $SiCl_4$ (b) SiH_2Cl_2
(c) $SiHCl_3$ (d) SiH_4
23. Semiconductors formed by the combination of elements of group III and VI or group II and VI are termed as
(a) Intermetallic semiconductors (b) Compound semiconductors
(c) Non – elemental semiconductors (d) All of the above

24. Semiconductors in which the ratio of positive and negative ions present in the compound differs from that required by the ideal chemical formula of the compound are
 (a) Elemental semiconductors (b) Non elemental semiconductors
 (c) Non-stoichiometric semiconductors (d) Stoichiometric semiconductors
25. Silicon crystals are doped by the following techniques
 (a) Diffusion (b) Ion implantation
 (c) Epitaxy (d) All of the above
26. A p - n junction diode is said to be forward biased if
 (a) Negative terminal of the battery is connected to n -type semiconductor and positive terminal of the battery is connected to the p -type semiconductor
 (b) Positive terminal of the battery is connected to n -type semiconductor and negative terminal of the battery is connected to the p -type semiconductor
 (c) Both negative and positive terminals of the battery is connected to n -type semiconductor
 (d) Both negative and positive terminals of the battery is connected to p -type semiconductor
27. The approximate superconducting transition temperature is mentioned against the materials. Which of the following is incorrect?
 (a) $\text{Ba}_x\text{La}_{2-x}\text{CuO}_4$ (35 K) (b) Nb_3Ge (23 K)
 (c) Y-Ba-Cu oxide (90 K) (d) Y-Ba-Cu oxide (300 K)
28. In the structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor the atoms situated at the body centre are
 (a) Ba and Cu (b) Cu and O
 (c) Y and Ba (d) Y and Cu
29. Which of the magnetic properties finds maximum usage in most of the engineering devices
 (a) Ferromagnetic and ferrimagnetic (b) Diamagnetic and paramagnetic
 (c) Paramagnetic and antiferromagnetic (d) Diamagnetic and ferromagnetic
30. Which of the following is not a ferromagnetic material
 (a) Iron (b) Zirconium
 (c) Cobalt (d) Nickel

Solutions

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (c) | 2 (b) | 3 (a) | 4 (a) | 5 (c) | 6 (b) | 7 (a) | 8 (a) |
| 9 (a) | 10 (b) | 11 (c) | 12 (b) | 13 (c) | 14 (b) | 15 (c) | 16 (a) |
| 17 (d) | 18 (c) | 19 (c) | 20 (d) | 21 (a) | 22 (c) | 23 (d) | 24 (c) |
| 25 (d) | 26 (a) | 27 (d) | 28 (c) | 29 (a) | 30 (b) | | |

Chapter 12

LIQUID CRYSTALS

12.1 Introduction

A crystal is a solid substance in which the atoms occupy definite positions called lattice points. When these solids are heated, the atoms leave their lattice positions and the solid changes into a liquid. In a liquid, atoms are randomly oriented. In some molecules in between these two stages there is an intermediate state in which although the solid acquires a tendency to flow like a liquid, the atoms are still arranged parallel to one another like that in a solid, that is, the degree of order is intermediate between that of a solid and a liquid. They are less ordered than a solid and more ordered than a liquid. This intermediate state is termed as the *liquid crystal* state or the *mesophase*. Liquid crystal is regarded as the fourth phase of matter (the other three phases being solid, liquid and gas).

The study of liquid crystals dates back to the year 1888, when it was observed by an Austrian botanist named Friedrich Reinitzer that cholesteryl benzoate has two distinct melting points. He observed that when cholesteryl benzoate is heated, it changes into a very viscous cloudy liquid at a more or less sharp characteristic temperature called the transition temperature. On further increasing the temperature, the cloudiness disappears again sharply at a new temperature called the melting point of the solid. Beyond the melting point, it behaves like an ordinary liquid. However, between the transition point and the melting point, the substance exhibits the fluidity of a liquid and the optical properties of a solid crystal.

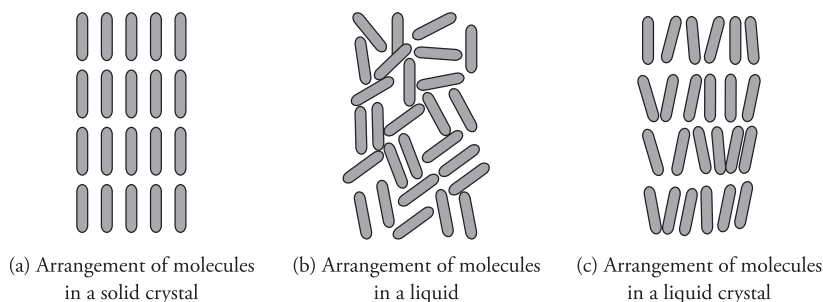


Figure 12.1 Arrangement of molecules in (a) solid crystal, (b) liquid and (c) liquid crystal

12.2 Characteristics of Liquid Crystals

All molecules do not acquire the liquid crystal state. Molecules that are oblong and rod shaped with rigidity along the long axis tend to acquire the liquid crystalline state. These molecules are generally elongated and shaped like a cigar. Some typical examples of liquid crystals are

- Cholesterol myristate/cholesteryl myristate
- Phenylbenzoates
- Glycolipids
- Cellulose derivatives
- Paraffins
- Surfactants

Apart from having a rod-like structure, liquid crystals can also be disc-like. The rod-like structures are called calamitic and the disc-like structures are called discotic. Calamitic liquid crystals are made up of two or more aromatic or aliphatic rings connected in one direction (Fig. 12.2).

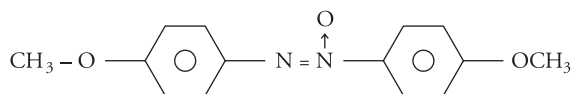


Figure 12.2 *p*-azoxyanisole (PAA) – rod-like calamitic crystal

In discotic liquid crystals, the mesogen is a rigid disc-like part (Fig. 12.3). There is a two-dimensional order in the molecules of a discotic crystal.

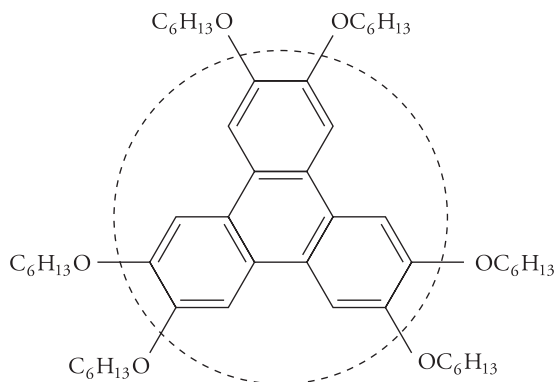


Figure 12.3 Disc-like (discotic) crystal

Molecules in any condensed phase generally have two types of orders.

- **Positional order:** Positional order may be defined as the tendency of molecules to occupy fixed positions.
- **Orientalional order:** It may be defined as the tendency of molecules to orient in a particular direction.

Crystalline solids have both positional and orientational order, that is, they occupy their fixed positions and are also aligned along a particular direction. Liquids have neither positional nor orientational order. Liquid crystals are crystals which have lost their positional order but maintain their orientational order. They point more in one direction over other directions and this direction is referred to as the *director* of the liquid crystals. Liquid crystals are anisotropic materials – their properties depend on the direction in which the measurement is made. They are also *birefringent* – they possess two different indices of refraction, one corresponding to the light polarised along the director and the other perpendicular to the director.

12.3 Classification of Liquid Crystals

Liquid crystals can be classified as *thermotropic liquid crystals* and *lyotropic liquid crystals*.

In thermotropic liquid crystals, the transition to the liquid crystalline state is temperature-dependent, whereas in lyotropic liquid crystals, the transitions are dependent on the concentration of the mesogens in the solvent. Thermotropic liquid crystalline state can be obtained in two ways.

- If a liquid crystalline state is obtained both by raising the temperature of a solid or lowering the temperature of a liquid, then such crystals are called *enantiotropic liquid crystals*.
- If the liquid crystalline state is attained from one direction only, that is, either by raising the temperature of a solid or by lowering the temperature of liquid, then such crystals are termed as *monotropic liquid crystals*.

Thermotropic liquid crystals find widespread application in technical fields, whereas lyotropic crystals are important for biological systems, such as, membranes.

Thermotropic crystals are of three types – nematic, cholesteric and smectic.

- Nematic liquid crystals** These crystals lack positional and translational order but have a remarkably long range orientational order (Fig. 12.4). All the molecules are oriented along a preferred axis termed as the director axis and appear to move together like swarms of mobile threads or straws (nematic is from the Greek word *nema* meaning thread). The molecules move either sideways or up and down. Each molecule can also twist or rotate around its axis giving rise to a twisted nematic. Since the molecules are oriented in one direction, they exhibit anisotropy. The fluidity of nematic crystals is like ordinary isotropic liquids but they are readily aligned in the same direction in the presence of electric and magnetic fields. The alignment of molecules is temperature sensitive – as the temperature is increased, the degree of orientation of the nematic crystals decreases and they change into isotropic liquids. Examples of compounds yielding nematic type liquid crystals are p-azoxyphenetole, anisaldazine,

p-methoxycinnamic acid, p-azoxyanisole, etc. Their transition and melting points are given in Table 12.1.

Table 12.1 Transition point and melting point of a few nematic type liquid crystals

Compound	Transition point (K)	Melting point (K)
p-azoxyphenetole	410	440
Anisaldazine	438	453
p-methoxycinnamic acid	443	459
p-azoxyanisole	389	408

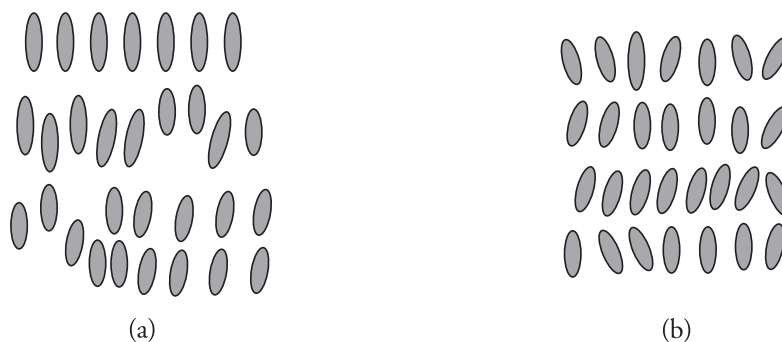


Figure 12.4 Nematic liquid crystals

- (ii) **Cholesteryl liquid crystals** This type of mesophase is formed by derivatives of cholesterol such as cholesteryl esters. Like the nematic phase, the molecules in this type of crystal are also parallel to each other but arranged in layers. The molecules in successive layers are slightly twisted or rotated with respect to the layers above and below so as to form a continuous helical or spiral pattern. Pitch is an important characteristic of this mesophase and may be defined as the distance taken by the director to rotate one full turn in the helix (Fig. 12.5). It depends on temperature – as the temperature increases, the pitch of the helix decreases.

Cholesteryl crystals form non-superimposable mirror images and can rotate the plane of polarised light to the right or left. Hence, they are also termed as chiral nematic phase. The rotatory power of these crystals is a thousand times greater than that of solid crystals like quartz. Cholesteryl benzoate, the first known liquid crystal, is of cholesteric type. Its transition temperature is 146 °C and melting point is 178.5 °C.

These crystals have the ability to selectively reflect light of wavelength equal to their pitch length. Hence, a colour will be reflected when the pitch is equal to the corresponding wavelength in the visible spectrum. It may be noted that cholesteryl crystals always exhibit the same colour at the same temperature. This property finds use in thermometers.

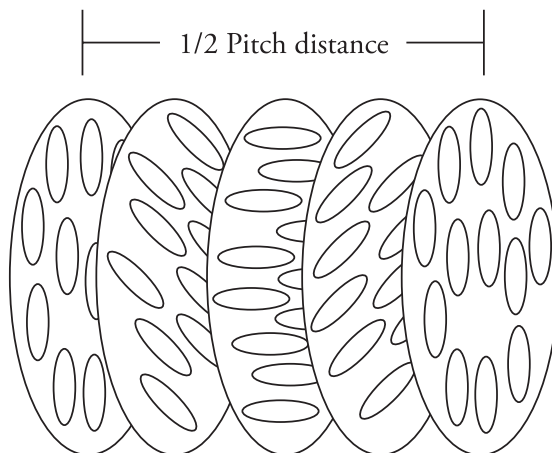


Figure 12.5 Pitch of a helix of cholesteral liquid crystal

- (iii) **Smectic liquid crystals** (Smectic is the Greek word for soap) The molecules in smectic crystals are oriented parallel to each other as in the nematic phase but in layers. These layers can slide past each other because the force between the layers is weak. Common soaps exhibit smectic state at high temperatures ($\approx 200^\circ\text{C}$) or in the presence of water. Liquid crystals do not flow like ordinary liquids – they flow in layers.

Many smectic structures have been reported in literature. They are denoted by alphabet letter A, B, C, etc. Some common types of smectic liquid crystals are given below.

- (a) **Smectic A** In smectic A, the molecules are aligned perpendicular to the layer planes.
 (b) **Smectic C** The arrangement of molecules is similar to smectic A except that the molecules are slightly tilted.

Smectic liquid crystals exhibit long range orientational order. They have high viscosity and are not suitable for devices.

Figure 12.6a–c shows the three types of thermotropic crystals.

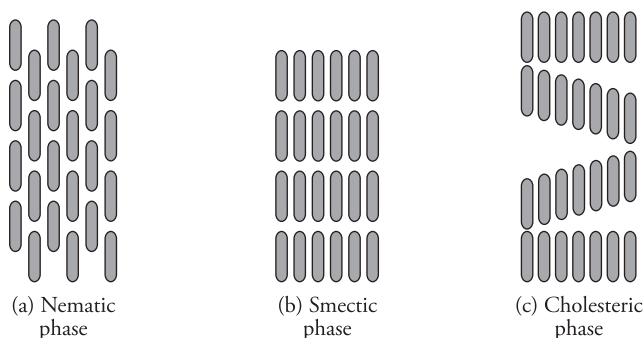


Figure 12.6 Different types of thermotropic crystals

Lyotropic liquid crystals The orientational behaviour of lyotropic crystals is a function of concentration and solvent. Common examples of lyotropic liquid crystals are soaps. These molecules are amphiphilic – they have both hydrophilic and hydrophobic ends in their molecules. The hydrophilic end is attracted towards water, whereas the hydrophobic end is water repellent and attracted towards non-polar solvents. At low concentrations, these molecules are randomly oriented but as the concentration increases, the molecules start arranging themselves. The hydrophobic heads point in one direction and their tails point in the other direction (Fig. 12.7).

Lyotropic liquid crystals are very common in living systems. Cell membranes and cell walls are examples of lyotropic liquid crystals. Phospholipid molecules are arranged perpendicular to the membrane surface. Soaps and detergents form lyotropic crystals when they combine with water.

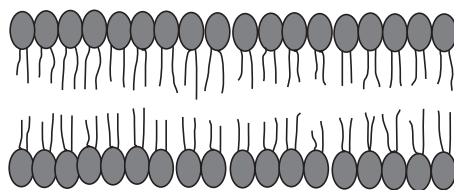


Figure 12.7 *Lyotropic liquid crystal*

Applications of liquid crystals Liquid crystals have widespread applications in the field of science and technology. Their anisotropic optical properties make them very useful in various devices. The change in orientation of these molecules in the presence of electric, magnetic and optical field leads to a number of magneto-optical, electro-optical and opto-optical effects.

The electro-optical effect of liquid crystals is widely used in wrist watches, pocket calculators, flat screens of laptops, LCDs, computers and televisions. They are also used in panel meters and a number of industrial products.

- (i) **Liquid crystal displays** Liquid crystal displays (LCD) are one of the most common and popular applications of liquid crystals. The use of these displays has increased very rapidly in recent years because of its manifold advantages. The liquid crystal display makes use of the optical properties of liquid crystals in the presence or absence of electric fields. They have low power consumption and greater clarity of display in the presence of bright light. Moreover, LCDs are much thinner than cathode ray tubes (CRTs) and work on the principle of blocking light rather than emitting it.
- (ii) **Thermometers** As discussed earlier (see cholesteric crystals, Section 12.3), cholesteric crystals show variation in colour with temperature. These crystals are highly sensitive to change in ambient temperature and show a particular colour at a specific temperature. Hence by simply looking at the colour, one can find the temperature of the device. Cholesteric crystals are able to record temperature variations of less than 0.01 °C. This property is utilized in making liquid crystal thermometers which are calibrated according to colour shown at different temperatures. These thermometers are highly sensitive and find use in medical and electronic fields. In the medical field, they are used to detect tumours, infections and are also used to locate arteries and veins as these vessels are warmer than the surrounding tissues. In

the electronic industry, they find use in locating faults in circuits, condition of batteries and so on by detecting the high temperature in faulty areas.

- (iii) **Radiation and pressure sensors** The colour changing ability of cholesteric crystals with temperature finds use in radiation and pressure sensors. When an invisible radiation falls on a device it brings about local change in temperature which can be easily registered. This principle is used in making sensors for detecting ultraviolet, infrared, microwave, ultrasonic and other ionizing radiations. Similarly, liquid crystal pressure sensors can also be made.
- (iv) **Optical imaging** Cholesteric liquid crystals are used in holography for recording and reconstructing the wave front emanating from a light source. In this technique, the image is recorded by placing a liquid crystal cell between the two layers of a photoconductor. When light falls on the photoconductor, an electric field corresponding to the intensity of light develops in the liquid crystal. This electric pattern is transmitted to the electrode which then records the image.
- (v) **Electronic paper** It is a display medium that has the properties of paper but can be reused many times. Electronic paper is thin, flexible, makes use of liquid crystals and can be read in illuminated environments. The information written on it can be stored and generally read without the use of power. Examples include electronic newspapers.
- (vi) **In research work** Nematic liquid crystals have been used for structure elucidation of compounds using NMR spectroscopy. The compound under study is dissolved in an anisotropic environment of nematic liquid crystal solvents. The structure of the compound can be determined from the values of chemical shift, dipole–dipole interaction, spin–spin coupling etc. Liquid crystals are also used as solvents in chromatographic techniques for separation of mixtures and find use in the study of molecular rearrangement and kinetics. They are also used as anisotropic solvents in visible, UV and IR spectroscopy of organic molecules.

Other applications Low molecular mass (LMM) liquid crystals are used for making erasable optical discs, full colour ‘electronic slides’ for computer aided drawing (CAD) and light modulators for colour electronic imaging. It is also used for visualizing radio frequency waves in wave guides.

- (vii) **Lyotropic liquid crystals** also have widespread applications. The commonest example of this type of crystal is the household soap. These crystals are amphiphilic; a part of these crystals dissolves in polar solvents and a part is soluble in non-polar solvents. This property can be used for various applications
 - They help in removing residual oil from a depleted oil well.
 - In the medical field, certain drugs are coated with lyotropic crystals to prevent them from being destroyed in the digestive tract.
 - Some liquid crystals are used in topical medications because certain drugs are more soluble in lyotropic liquid crystals than in water. For example, hydrocortizone has limited applications because the highest possible concentration is only 1%. However, when the drug is blended into a liquid crystal of lecithin and water its concentration increased to 4%.
 - Lyotropic liquid crystals are used to make stable hydrocarbon foam.

(viii) Liquid crystal in biological systems The liquid crystal state is found in a large number of biological systems. Mesomorphic compounds are found in the kidneys, liver, brain, spleen, etc. They exist as sterol and lipid derivatives. The mesomorphic state is also shown by certain living sperms, solution of tobacco mosaic virus (TMV), collagen, haemoglobin of sickle cell anemia, nucleic acid, fibrinogen, etc.

Summary

- Liquid crystals are regarded as the fourth phase of matter (the other three phases are liquid, solid and gaseous).
- Liquid crystals have properties intermediate between solid and liquid. They can flow like liquids but the molecules remain arranged like that in solids.
- The molecules forming the liquid crystalline state are generally elongated and rod-shaped (calamitic); however, they can also have a two-dimensional order and be arranged in columns or discs (columnar or discotic).
- Those molecules in which transition to a liquid crystalline state is temperature-dependent are called thermotropic liquid crystals.
- Those molecules where transition to a liquid crystalline state is dependent on concentration or solvent are called lyotropic liquid crystals.
- Thermotropic liquid crystals are of three types:
 - (i) Nematic: All the molecules are oriented along a preferred axis called the director axis and they appear to move together like swarms of mobile threads.
 - (ii) Cholesteryl liquid crystals: The molecules are arranged like nematic crystals but in layers. Molecules in successive layers are slightly twisted or rotated with respect to the layers above and below, and they form a spiral or helical pattern.
 - (iii) Smectic liquid crystals: In these crystals also, the molecules are oriented like nematic crystals but in layers such that one layer can slide past the other layer.
- Thermotropic liquid crystals find use in liquid crystal displays, liquid crystal thermometers, radiation and pressure sensors, optical imaging and have numerous applications in research.
- Lyotropic liquid crystals are generally found in biological systems.

Review Questions

1. What are liquid crystals? Explain.
2. Define liquid crystals and classify them.
3. Write short notes on
 - (a) Thermotropic liquid crystals
 - (b) Lyotropic liquid crystals

- (c) Nematic liquid crystals
 - (d) Cholesteryl liquid crystals
 - (e) Smectic liquid crystals
4. Explain in detail the various applications of liquid crystals.

Multiple Choice Questions

1. The fourth state of matter is
 - (a) Glassy state of matter
 - (b) Liquid crystal state
 - (c) Micellar state
 - (d) Metastable state
2. Liquid crystals exhibit properties intermediate between
 - (a) Solid–liquid state
 - (b) Liquid–gaseous state
 - (c) Solid–gaseous state
 - (d) None of the above
3. Liquid crystalline properties were first observed in
 - (a) Cholesteryl benzoate
 - (b) α -lecithin
 - (c) Sodium stearate
 - (d) Cholesteryl nonanoate
4. Which is not an example of thermotropic liquid crystals?
 - (a) p- azoxyanisole (PAA)
 - (b) Cholesteryl benzoate
 - (c) Sodium stearate
 - (d) Cholesteryl myristate
5. Liquid crystals that find use in the manufacture of liquid crystalline thermometers are –
 - (a) Nematic crystals
 - (b) Lyotropic crystals
 - (c) Smectic crystals
 - (d) Cholesteryl crystals
6. Liquid crystals in which the molecules are oriented parallel to each other in layers and the adjacent layers can slip past each other are
 - (a) Nematic liquid crystals
 - (b) Smectic liquid crystals
 - (c) Cholesteryl liquid crystals
 - (d) Lyotropic liquid crystals
7. Which of the following is not an example of lyotropic liquid crystals?
 - (a) α -lecithin
 - (b) Sodium stearate
 - (c) p-azoxyanisole (PAA)
 - (d) Phospholipids
8. Liquid crystals having chiral centre are
 - (a) Cholesteryl liquid crystals
 - (b) Nematic liquid crystals
 - (c) Smectic liquid crystals
 - (d) Lyotropic liquid crystals
9. Liquid crystals that form a helical or spiral structure are
 - (a) Smectic liquid crystals
 - (b) Cholesteryl liquid crystals
 - (c) Nematic liquid crystals
 - (d) All of the above

10. Liquid crystals have widespread applications in

- | | |
|------------------------------------|-------------------|
| (a) Liquid crystal displays | (b) Thermometers |
| (c) Radiation and pressure sensors | (d) All the above |

Solutions

- | | | | | |
|-------|-------|-------|-------|--------|
| 1 (b) | 2 (a) | 3 (a) | 4 (c) | 5 (d) |
| 6 (b) | 7 (c) | 8 (a) | 9 (b) | 10 (d) |

Chapter 13

CHEMICAL KINETICS

13.1 Introduction

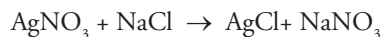
The study of chemical reactions has been of great interest to the chemists. They wish to investigate the manner in which the reaction occurs and the speed at which it takes place. They are also interested in studying the effect of various parameters like temperature, pressure and concentration on the rate of the reaction. Chemical kinetics deals with all the above and can be defined as the branch of chemistry which deals with

- The rate of chemical reaction
- The mechanism by which the reactants are converted into products and
- The factors affecting the rate of a reaction

It is observed that different reactions occur at different rates. Some reactions are fast and some reactions occur very slowly and take months or even years for their completion, while some reactions occur at a moderate rate. It is these reactions occurring at moderate speed which are of great interest to the chemists, as their rates can easily be measured in the laboratory.

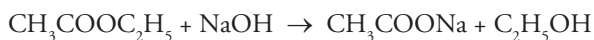
Depending upon their speed, the chemical reactions are categorised as follows

1. **Fast reactions** Reactions that occur instantaneously as soon as the reactants are mixed together are termed as fast reactions, for example, the precipitation of the solution of silver nitrate and sodium chloride.



Similarly, neutralisation of acid and base also occurs as soon as the two substances are mixed. Generally, ionic reactions are fast reactions because they involve ions that are held together by electrostatic forces and no bonds are broken in them. The rates of these reactions are too fast to be determined by conventional methods. These methods cannot deal with reactions whose half-lives are less than a second or so. Special techniques are employed to measure the rate of such reactions.

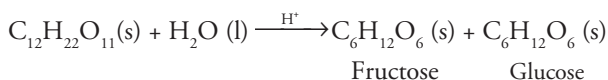
2. **Very slow reactions** Some reactions like rusting of iron occur so slowly that one can be misled into thinking that no reaction is occurring at all. These reactions proceed very slowly and it becomes difficult to determine the speed of the reactions.
3. **Moderate reactions** These reactions occur in a conveniently measurable time and their rates can be measured easily in the laboratory. Examples of such reactions are
 - (i) Hydrolysis of ester in presence of sodium hydroxide.



- (ii) Decomposition of hydrogen peroxide.



- (iii) Inversion of cane sugar in aqueous solution.

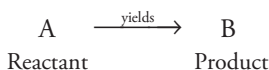


In general, *very fast reactions* are completed in microseconds or less with their half-life ranging from 10^{-12} to 10^{-6} s. *Fast reactions* are completed in seconds and their half-life ranges from 10^{-6} to 1 second. *Moderate reactions* with a half-life of 1 to 10^3 s are completed in minutes or even hours. *Slow reactions* take weeks for completion and their half-life spans from 10^3 to 10^6 s. Last of all, reactions which are completed in weeks or even years are termed as *very slow reactions* which have a half-life greater than 10^6 s.

13.2 Rate of Reaction

As the chemical reaction proceeds, the concentration of reactants and products changes continuously with time. The concentration of reactant decreases with time and that of the product increases with time. This change of concentration of either reactants or products per unit time is termed as the rate of a reaction. The velocity of a reaction is measured either in terms of the rate of decrease in concentration of reactants or the rate of increase in concentration of products.

Consider the following hypothetical reaction:



As time passes, the concentration of A goes on decreasing and the concentration of B goes on increasing.

The rate of the reaction may be expressed as

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of A}}{\text{Time taken}}$$

$$\text{Rate of reaction} = \frac{\text{Increase in concentration of B}}{\text{Time taken}}$$

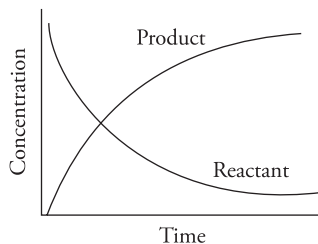


Figure 13.1 Variation of concentration of reactants /products with time

If $\Delta[A]$ is the decrease in the concentration of reactant A in time $\Delta[t]$ and $\Delta[B]$ is the increase in the concentration of B in the same time duration then the change in the concentration of reactants and products during a time interval $\Delta[t]$ can also be expressed as

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t}$$

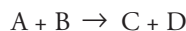
or
$$\text{Rate of reaction} = +\frac{\Delta[B]}{\Delta t}$$

The square brackets express the molar concentration (mol/L) of the reactants or products. The value of $\Delta[A]$ will be negative as the concentration of reactants is decreasing with time ($\Delta[A] = \text{Final concentration of A} - \text{initial concentration of A}$). This would make the rate of reaction $\frac{\Delta[A]}{\Delta t}$ negative. However, the rate of a reaction cannot be a negative quantity; therefore, a minus sign is put before $\Delta[A] / \Delta t$ so that the rate becomes positive. The minus sign simply indicates that as time increases, the concentration of the reactant A decreases. Thus,

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

In the above example, the stoichiometric coefficients of A and B are the same. Therefore, the rate of decrease in the concentration of A is equal to the rate of increase in the concentration of B.

Consider another reaction:

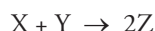


The rate of the reaction may be expressed by any one of the following expressions:

$$-\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = +\frac{\Delta[C]}{\Delta t} = +\frac{\Delta[D]}{\Delta t}$$

The rate of reaction when the stoichiometric coefficients of reactant and products are different

Consider the reaction



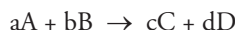
In the above example, one mole of X reacts with one mole of Y to give two moles of Z. This means that the rate of disappearance of X is equal to the rate of disappearance of Y, but the rate of appearance of Z is twice the rate of disappearance of either X or Y. Thus,

$$2 \times \text{Rate of disappearance of X} = 2 \times \text{Rate of disappearance of Y} = \text{Rate of appearance of Z}.$$

Therefore, the rate of reaction for such reactions is obtained by dividing each concentration term by its coefficient in a balanced chemical equation. Hence, for the above reaction

$$\text{Rate of reaction} = -\frac{\Delta[X]}{\Delta t} = -\frac{\Delta[Y]}{\Delta t} = +\frac{1}{2} \frac{\Delta[Z]}{\Delta t}$$

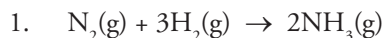
For a general reaction,



The rate of reaction

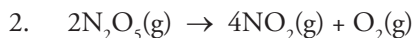
$$-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Other examples are



The rate of reaction

$$= -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$$



The rate of reaction

$$= -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = +\frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = +\frac{\Delta[\text{O}_2]}{\Delta t}$$



The rate of reaction

$$= -\frac{1}{2} \frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

13.3 Average Rate and Instantaneous Rate

The rate expressions discussed so far give the average rate of reactions over a time interval (Δt). This may be expressed as

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Time interval}} = \frac{\Delta[x]}{\Delta t}$$

The average rate of a reaction gives us the rate of a reaction over a particular time interval. As the reaction rate depends upon the concentration of the reactants, which is continuously decreasing with time, it is not possible to find the rate of the reaction at a particular time with the help of the expression of average reaction rate. For this purpose, the rate of a reaction is expressed as the instantaneous rate which measures the rate of a reaction at a specific time t . It is obtained by making the time interval (Δt) as small as possible so that Δt shrinks to a point. As Δt becomes smaller and smaller, (Δx) also becomes small. In the limiting case when Δt approaches zero, $\frac{\Delta[x]}{\Delta t}$ approaches the instantaneous reaction rate at time t . Therefore, instantaneous reaction rate equals the limiting value of the ratio $\frac{\Delta[x]}{\Delta t}$ as Δt approaches zero. It can be determined by drawing a tangent to the curve at a point corresponding to the given time. The slope of the tangent gives the rate of reaction at that time. The instantaneous rate may be represented by $-\frac{d[A]}{dt}$ or $\frac{d[B]}{dt}$ instead of $-\frac{\Delta[A]}{\Delta t}$ or $+\frac{\Delta[B]}{\Delta t}$, respectively.

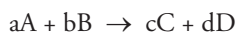
Mathematically,

$$\left[\frac{\Delta[A]}{\Delta t} \right]_{\Delta t \rightarrow 0} = \frac{d[A]}{dt} \quad \text{and} \quad \left[\frac{\Delta[B]}{\Delta t} \right]_{\Delta t \rightarrow 0} = \frac{d[B]}{dt}$$

In general, if dx represents infinitesimally small change in concentration of reactants or products in infinitesimally small time. The rate of the reaction may be expressed as:

$$\text{Rate of reaction} = \frac{dx}{dt}.$$

For a general reaction,



The rate of reaction

$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

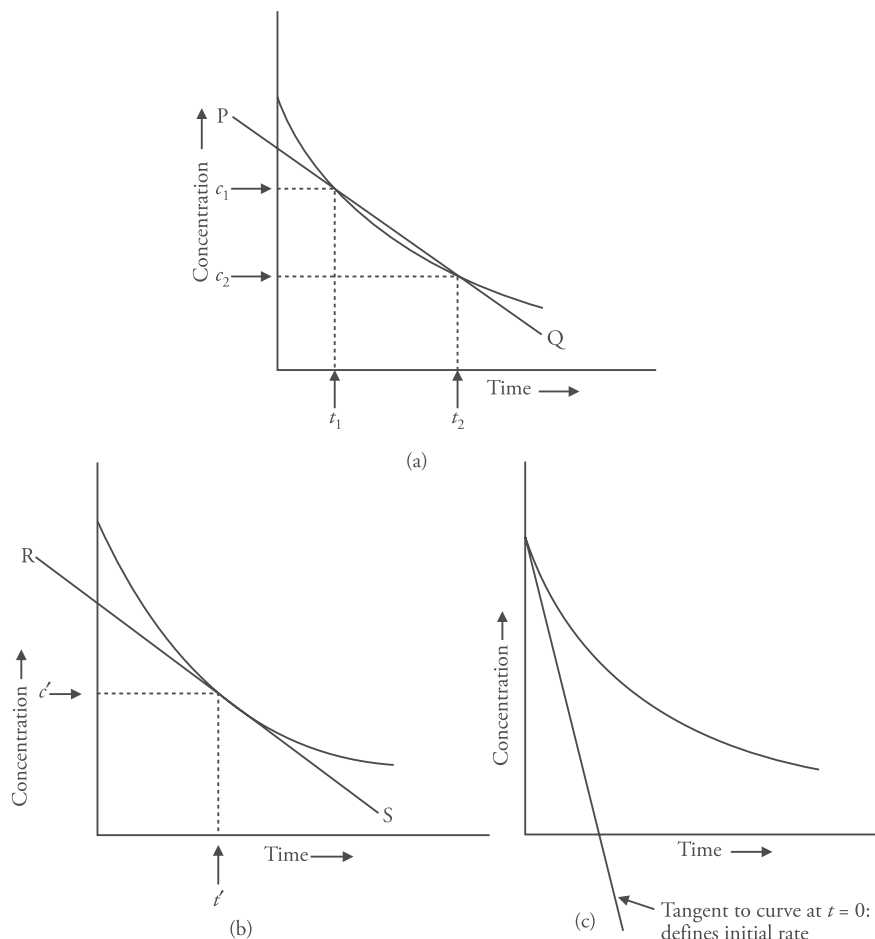
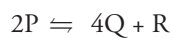


Figure 13.2 Concentration vs time graph illustrating (a) average rate, (b) instantaneous rate and (c) initial rate

Solved Examples

- Consider a chemical reaction $2P \rightleftharpoons 4Q + R$. The reaction occurs in gaseous phase in a closed vessel. The concentration of Q is found to increase by 8×10^{-3} mol/L in 10 s. Calculate (i) the rate of appearance of Q and (ii) the rate of disappearance of P.

Solution



$$\text{The rate of reaction} = -\frac{1}{2} \frac{d[P]}{dt} = +\frac{1}{4} \frac{d[Q]}{dt}$$

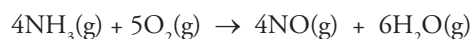
- (i) According to the equation, $d[Q] = 8 \times 10^{-3} \text{ mol/L}$ $dt = 10 \text{ s}$

$$\text{Rate of appearance of Q} = \frac{1}{4} \times \frac{8 \times 10^{-3}}{10} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(ii) -\frac{1}{2} \frac{d[P]}{dt} = +\frac{1}{4} \frac{d[Q]}{dt}$$

$$= \frac{d[P]}{dt} = \frac{2}{4} \times \frac{8 \times 10^{-3}}{10} = 4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

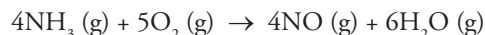
2. The reaction of ammonia and oxygen occurs at high temperature as follows



If the rate of formation of NO is $4.8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, calculate

- (i) the rate of disappearance of ammonia and (ii) the rate of formation of water.

Solution



$$\text{Rate of reaction} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

- (i) Rate of disappearance of ammonia

$$\text{Rate of disappearance of NH}_3 = \text{Rate of appearance of NO}$$

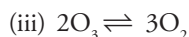
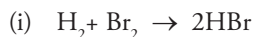
$$= 4.8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{Rate of formation of water} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} = \frac{1}{4} \frac{d[\text{NO}]}{dt}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = \frac{6}{4} \times 4.8 \times 10^{-3} = 7.2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}.$$

Practice Problems

1. Express the rate of the following reactions in terms of concentration of reactants and products



$$\text{Ans (i) } -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{Br}_2]}{dt} = \frac{1}{2} \frac{d[\text{HBr}]}{dt}$$

$$\text{(ii) } -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{Cl}_2]}{dt} = \frac{1}{2} \frac{d[\text{NOCl}]}{dt}$$

$$\text{(iii) } -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt}$$

2. For the reaction

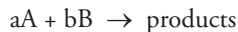
$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, the rate of the reaction measured as $\frac{\Delta[\text{NH}_3]}{\Delta t}$ was found to be $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. Calculate the rate of reaction expressed in terms of (i) N_2 and (ii) H_2 .

[Ans (i) $1.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$, (ii) $3.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$]

13.4 Rate Law Expression

It is the mathematical relation between the rate of the reaction and the concentration of the reacting species.

Consider a general reaction



where A and B are reactants and a and b are the stoichiometric coefficients of the balanced equation.

From the kinetic study of the reaction, the dependence of rate of the reaction on the concentration of the reactants is found to be

$$\text{Rate} = k [\text{A}]^p [\text{B}]^q$$

p and q are the powers of the reactants A and B on which the rate of the reaction depends and k is the rate constant. It may be noted that p and q are determined experimentally and may or may not be equal to the coefficients a and b in the reaction.

Consider the reaction,

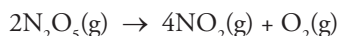


The rate law for the above reaction is

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

In the above example, a and b are equal to p and q .

Similarly, consider the decomposition of dinitrogen pentoxide



Experimental studies have shown that the rate of the reaction is proportional to $[\text{N}_2\text{O}_5]$ and not to $[\text{N}_2\text{O}_5]^2$.

Therefore, the rate law is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

In the above example, a and b are not equal to p and q .

13.5 Velocity Constant or Rate Constant

Consider a reaction $\text{A} + \text{B} \rightarrow \text{products}$. The rate of the reaction is given by

$$\text{Rate} \propto [\text{A}][\text{B}]$$

$$\text{Rate} = k [\text{A}][\text{B}]$$

Here k is the proportionality constant known as the velocity constant or the specific reaction rate of a reaction at a given temperature.

If $[\text{A}] = [\text{B}] = 1$ then in the above equation, $\text{Rate} = k$

Hence, velocity constant of a reaction at a given temperature can be defined as the rate of the reaction when the concentration of each of the reactants is unity.

Characteristics of rate constant

1. Rate constant is a measure of the reaction rate. Larger the value of k , faster is the reaction. Similarly, smaller value of k indicates slow reaction.
2. At a particular temperature, the rate constant of a particular reaction is fixed. Rate constant varies with the temperature of the reaction.
3. For a specific reaction, the rate constant does not depend on the concentration of the reacting species.

Table 13.1 Difference between rate of reaction and rate constant

Rate of reaction	Rate constant
1. It measures the speed of the reaction and can be defined as the rate of change of concentration of either reactants or products with time.	Rate constant is equal to the rate of the reaction when the concentration of each of the reactants is unity.
2. Initial concentration of the reactants affects the rate of the reaction	It is independent of the initial concentration of the reactants
3. Its unit is mol/L/time	The unit of rate constant depends on the order of the reaction

Units of rate constant

Consider a general reaction



$$\text{Rate of reaction, } dx/dt = k[A]^a[B]^b \quad (1)$$

$$\text{Unit of rate of reaction} = \text{mol/L/s} \quad (2)$$

$$\text{and } [A] \text{ and } [B] \text{ are mol/L} \quad (3)$$

Substituting (2) and (3) in (1), we get

$$\frac{\text{mol}}{\text{liter}} \times s^{-1} = k \left(\frac{\text{mol}}{\text{liter}} \right)^a \times \left(\frac{\text{mol}}{\text{liter}} \right)^b \times \dots$$

$$\begin{aligned} \text{or } k &= \left[\left(\frac{\text{mol}}{\text{liter}} \right)^{1-(a+b+\dots)} \times (s^{-1}) \right] \\ &= (\text{mol liter}^{-1})^{1-(a+b+\dots)} \times (s^{-1}) \\ &= (\text{mol})^{1-n} (\text{liter})^{n-1} (s^{-1}) \end{aligned} \quad (4)$$

$$(a + b + \dots = n)$$

n = order of the reaction

13.6 Factors Influencing Reaction Rate

The principal factors affecting the rate of the reactions are as follows:

1. Concentration of reactants
 2. Nature of reactants and products
 3. Temperature
 4. Catalyst
 5. Surface area
 6. Effect of radiations
1. **Concentration of reactants** Rate of reaction is directly proportional to the concentration of the reactants at a particular time. This is because when the concentration is high there is a greater probability of the molecules to collide with each other and form products. As the reaction proceeds further, the concentration of the reactants decreases, the collision frequency reduces and hence the rate of the reaction decreases.
 2. **Nature of reactants and products** During a chemical reaction bond cleavage and bond formation takes place, therefore the strength of these bonds and their environment in the reacting molecules will affect the rate of the reaction. For example, ionic reactions proceed almost instantaneously as they involve ionic species and no bonds are broken. Reactions

involving covalent bonds proceed rather slowly depending upon the strength of the bonds. Some reactions like rusting of iron proceed very very slowly.

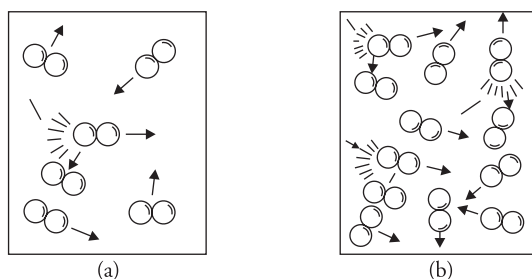


Figure 13.3 Concentration of reactant (a) slow reaction at low reactant concentration; (b) fast reaction at high reactant concentration

3. **Temperature of the system** Most of the chemical reactions are accelerated by the increase in temperature. It has been observed that the rate of reaction in a homogeneous reaction is approximately doubled for every 10 °C rise in temperature. The effect of temperature on reaction rates is discussed in detail in Section 13.13.
4. **Presence of catalyst** A catalyst is a substance that alters the rate of chemical reaction without itself undergoing any chemical change (Section 13.16). The action of catalyst is specific (i.e., only a particular catalyst can catalyse a particular reaction). For example, a mixture of H_2 and O_2 does not react at room temperature but the reaction proceeds vigorously when finely divided platinum is used as a catalyst. Similarly, hydrogenation of vegetable oils is catalysed by finely divided nickel.
5. **Surface area** Surface area of the reactants has a direct bearing on the rate of the reaction. Larger the surface area faster is the reaction. In case of solids the rate of reaction depends upon the state of subdivisions of the solid. For example, it is difficult to burn lumps of coal, but powdered coal burns very easily and vigorously.
6. **Effect of radiations** The reaction rates of certain reactions increase markedly when radiations of a specific wavelength are absorbed by the reacting molecules. For example, in absence of light the reaction of hydrogen and chlorine is very slow but the reaction proceeds very rapidly in the presence of sunlight.

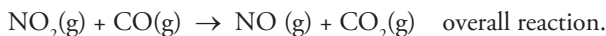
It is important to note that the rate of homogeneous reactions is affected by the first four factors. The rate of heterogeneous reactions depends upon the surface area, whereas radiations affect the rate of photochemical reactions. The effect of temperature and catalyst on reaction rates have been discussed in detail later in the chapter.

13.7 Reaction Mechanism

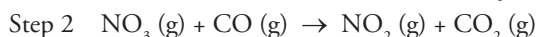
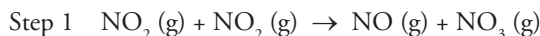
Till now, we have studied reaction rates. We have seen how the reaction rate varies with concentration of the reactants. Another important aspect of chemical kinetics is the series of steps

by which the reactant is transformed into products. *This series of steps by which a reactant changes into products is called the reaction mechanism.*

It has been observed that most reactions are not completed in a single step. They are completed in many steps. Every single step that contributes to the overall reaction mechanism is termed as the elementary step or the elementary reaction. This can be explained with the help of the reaction of nitrogen dioxide and carbon monoxide to produce nitric oxide and carbon dioxide in gaseous phase.

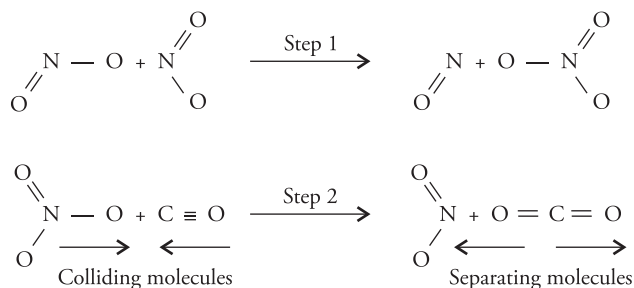


It has been proved experimentally that the above reaction takes place by a two-step mechanism



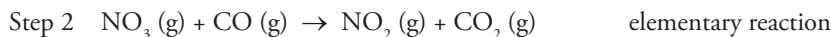
Steps 1 and 2 comprise the elementary steps or elementary reaction.

- In the first elementary step, oxygen atom from one NO_2 molecule is transferred to the other NO_2 molecule. This occurs when two NO_2 molecules with enough energy collide to break one N–O bond and form another.
- In the second elementary step, the NO_3 molecule formed in the first step transfers an oxygen atom to CO forming NO_2 and CO_2 .



Thus, we see that the chemical equation for an *elementary step describes the individual molecular events* in which the old bonds are broken and new bonds are formed. The overall reaction does not give any information about the mechanism of the reaction and simply expresses the stoichiometry of the overall process.

The elementary steps are summed up to obtain the overall reaction



From the above reaction mechanism, it can be seen that NO_3 formed in one step is consumed in the other step. It does not appear in the overall reaction. Such species that are formed and consumed in the reaction and do not appear in the final equation are termed as the reaction intermediate.

Elementary steps are classified in terms **molecularity**, which describes the number of reactant molecules or ions in each elementary step. As in the above example, two molecules react in both steps 1 and 2 to form products hence the molecularity of each elementary reaction is 2 (bimolecular).

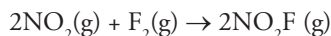
Reaction mechanism and rate law

In a multi-step reaction, each elementary step has a different reaction; therefore, each step will occur at a different rate. Some steps will be fast, whereas others will be slow. In such a case where all steps occur at different rates the rate of the overall reaction will be determined by the slowest step.

This can be understood by the following analogy. Consider that a car industry manufactures engines, brake parts, steering and seat at the rate of 30, 200, 100 and 250 pieces per day, respectively. The overall rate of production of cars cannot be more than 30 per day, which depends on the production of the slowest working section of the factory.

Thus, the slowest step in the mechanism determines the overall rate of a chemical reaction. This slowest step is termed as the rate-determining step.

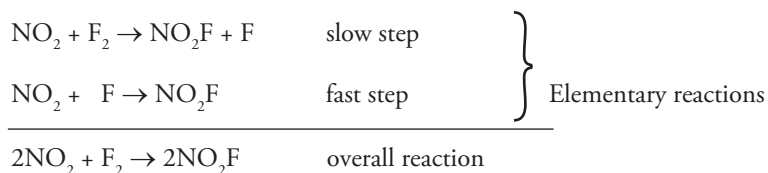
Let us consider the example of reaction between NO_2 and F_2 reacting to form NO_2F .



Experimentally, the rate of the reaction is given by the rate equation

$$\text{Rate} = k [\text{NO}_2] [\text{F}_2]$$

The above-mentioned rate equation indicates that only one NO_2 molecule reacts with F_2 in the rate-determining step. Hence, the following mechanism can be suggested



Rate law expression for reactions involving equilibrium

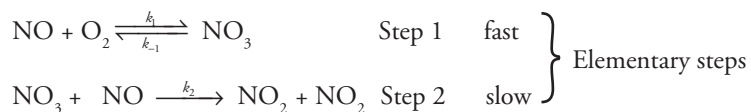
There are many reactions in which the first step involves equilibrium and produces an intermediate. The intermediate then reacts slowly to give the products.

Consider the reaction of NO and O_2 to produce NO_2 .

Experimentally, the rate of the reaction is given by

$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$$

In view of the above rate law expression, the following mechanism is proposed



k_1 and k_{-1} are the rate constants of forward and backward reactions, respectively.

k_2 = rate constant for step 2

The second step in the reaction being the slowest step determines the rate of the reaction

$$\text{Rate} = k_2[\text{NO}_3][\text{NO}] \quad (\text{i})$$

Concentration of NO_3 is obtained by steady-state treatment, which states that

Rate of formation of $[\text{NO}_3]$ = Rate of its removal

or the change in concentration of NO_3 with time is zero.

$$k_1[\text{NO}][\text{O}_2] = k_{-1}[\text{NO}_3] + k_2[\text{NO}_3][\text{NO}]$$

$$k_1[\text{NO}][\text{O}_2] = [\text{NO}_3]\{k_{-1} + k_2[\text{NO}]\}$$

$$[\text{NO}_3] = \frac{k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]} \quad (\text{ii})$$

Placing the value of $[\text{NO}_3]$ in Eq. (i), we get

$$\begin{aligned} \text{Rate} &= \frac{k_2[\text{NO}] \cdot k_1[\text{NO}][\text{O}_2]}{k_{-1} + k_2[\text{NO}]} \\ &= \frac{k_2 \cdot k_1[\text{NO}]^2[\text{O}_2]}{k_{-1}} \quad \text{since } k_2[\text{NO}] \ll k_{-1} \\ &= k'[\text{NO}]^2[\text{O}_2] \quad \text{where } k' = k_2 \cdot k_1 / k_{-1} \end{aligned}$$

13.8 Order and Molecularity of Reaction

A large number of reactants may take part in product formation but the rate of the reaction may or may not depend on the concentration of all the reactants taking part in the formation of products. The concentration terms, which affect the reaction rate, signify the order of the reaction that may be defined as the 'total number of atoms, ions or molecules whose concentration actually alters the rate of the reaction'.

It is an experimental quantity and can be obtained by adding the powers to which the concentration terms are raised in a rate law expression.

Thus, for a general reaction:



If the rate law is

$$\text{Rate} = -\frac{dx}{dt} = k [A]^p [B]^q [C]^r$$

Then the order of the reaction 'n' is

$$n = p + q + r$$

where p is the order of reaction wrt A, q is the order of reaction wrt B and r is the order of reaction with respect to C. The overall order of the reaction is given by $p + q + r$.

The reactions can be classified according to the order of a reaction into the following types:

- (a) **First-order reaction** A reaction in which the rate depends on a single concentration term is termed as a first-order reaction.



$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

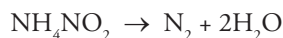
Examples

- (i) Decomposition of nitrogen pentoxide (N_2O_5)



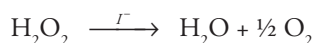
$$\text{Rate} = k [\text{N}_2\text{O}_5].$$

- (ii) Decomposition of ammonium nitrite in aqueous solution



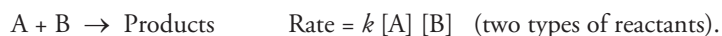
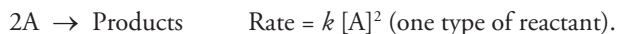
$$\text{Rate} = k [\text{NH}_4\text{NO}_2].$$

- (iii) Decomposition of H_2O_2 in the presence of I^- ions



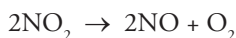
$$\text{Rate} = k [\text{H}_2\text{O}_2].$$

- (b) **Second-order reaction** It is defined as a reaction in which two concentration terms affect the rate of reaction.



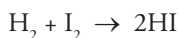
Examples are as follows

- (i) Decomposition of nitrogen peroxide:



$$\text{Rate} = k [\text{NO}_2]^2.$$

- (ii) Reaction between
- H_2
- and
- I_2
- to give HI



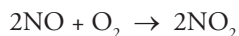
$$\text{Rate} = k [\text{H}_2] [\text{I}_2].$$

- (c)
- Third-order reaction**
- If the rate of the reaction is affected by three concentration terms, it is said to be a third-order reaction.



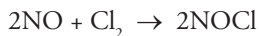
Examples are as follows:

- (i) Combination of nitric oxide and oxygen to form
- NO_2



$$\text{Rate} = k [\text{NO}]^2 [\text{O}_2].$$

- (ii) Combination of nitric oxide and
- Cl_2
- to form
- NOCl

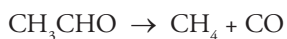


$$\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2].$$

- (d)
- Fractional-order reactions**
- When the exponent to which the concentration terms are raised is a fraction, it is known as fractional-order reaction

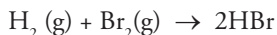
Examples are as follows:

- (i) Decomposition of acetaldehyde is a fractional-order reaction.



$$\text{Rate} = k [\text{CH}_3\text{CHO}]^{3/2} \quad \text{order} = 3/2 \text{ or } 1.5.$$

- (ii) Formation of
- HBr
- by the reaction between
- H_2
- and
- Br_2
- is a fractional-order reaction.



$$\text{Rate} = k [\text{H}_2] [\text{Br}_2]^{1/2} \quad \text{order} = 1 + 1/2 = 1.5.$$

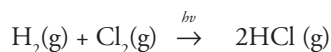
- (e) **Zero-order reaction** If the rate of a reaction does not depend on the concentration of the reactants, then it is said to be a zero-order reaction.



$$\text{Rate} = k[A]^0.$$

Examples are as follows:

Photochemical combination of H_2 and Cl_2 over water surface. Decomposition of ammonia on the surface of metals like gold and platinum is an example of zero-order reaction.



$$\text{Rate} = k.$$

Molecularity of a reaction

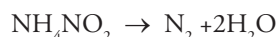
It is the total number of reactant molecules taking part in each elementary step of a chemical reaction.

The molecularity of each elementary step is obtained by adding the number of reactant molecules as expressed by a balanced chemical equation.

On the basis of molecularity, the reactions may be classified as follows:

- (a) **Unimolecular reaction** It is one in which a single molecule of reactant is involved.

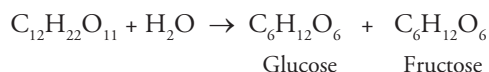
For example,



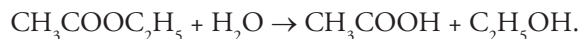
- (b) **Bimolecular reaction** These reactions involve collision of a pair of molecules. Bimolecular reactions are common.

Examples are as follows:

- (i) Inversion of cane sugar:

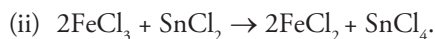


- (ii) Hydrolysis of ester:



- (c) **Termolecular reaction** It is one in which three molecules are involved:

For example,



(d) **Pseudo-unimolecular reactions**

Consider the reaction



The molecularity of the above reaction is two and it is a second-order reaction. The rate law is

$$\text{Rate} = k [A] [B].$$

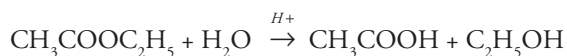
In the above reaction, if reactant B is present in large excess then its concentration does not change much during the course of the reaction. Thus, the concentration of B remains practically constant during the entire reaction. The rate law now becomes

$$\text{Rate} = k' [A] \text{ where } k' = k[B].$$

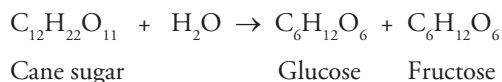
k' is a new rate constant known as pseudo-first-order rate constant and sometimes pseudo-unimolecular rate constant. The reaction is actually a second-order reaction, but in practice it is found to be a first-order reaction because one of the reactants is present in large excess. Such reactions are termed as pseudo-order or pseudo-molecular reactions. The above reaction will be a pseudo-first-order reaction.

Examples of pseudo-molecular reactions are as follows

(i) Hydrolysis of ethyl acetate.



(ii) Inversion of cane sugar



In both these reactions, large excess of water is used and hence its concentration remains almost constant during the reaction. Therefore, the reaction becomes first order with respect to $\text{CH}_3\text{COOC}_2\text{H}_5$ in (i) and $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in (ii).

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

Reactions like hydrolysis of ester or inversion of cane sugar, which, although bimolecular, follow first-order kinetics and are called 'pseudo-unimolecular reactions' or 'pseudo-first-order reactions'.

Table 13.2 Difference between order and molecularity

S.No.	Molecularity	Order
1	The number of reactant molecules taking part in each elementary step of a reaction is termed as its molecularity	It is the sum of powers of the concentration terms in a rate law expression
2	Molecularity is a theoretical concept	Order of a reaction is an experimental quantity

3	Molecularity is always a whole number, i.e., 1, 2, 3, etc. It can never be zero or fraction	Order of a reaction can be a whole number, a fraction or even zero
4	It can be obtained from balanced equation of a single reaction of known mechanism	It cannot be obtained from balanced or stoichiometric equation
5	Each elementary step of a reaction has its own molecularity	Order is for the overall reaction

13.9 Kinetic Equation of Different Orders/Integrated Rate Reactions

- (i) **Kinetics of zero-order reactions** If the rate of the reaction does not depend upon the concentration of the reactants, then the reaction is said to be a zero-order reaction. Alternatively, if the concentration of reactants remains unaltered during the reaction, it is a zero-order reaction.

Consider the reaction



Reaction rate is given by the differential rate equation:

$$= -\frac{d[A]}{dt} = k[A]_0 = k$$

This differential equation is converted into an integrated equation by simple mathematics:

Let 'a' be the initial concentration of the reactant A. At any instant if x is the amount of A transformed into product, then the rate of formation of product is given by:

$$\frac{dx}{dt} = k(a - x)^0 = k$$

Separating the variables and integrating

$$\int dx = k \int dt$$

$$x = kt + I \quad (1)$$

where I is the integration constant.

$$\text{When } t = 0 \quad x = 0 \quad (2)$$

Placing the value of x and t in Eq. (1) we get

$$I = 0 \quad (3)$$

$$\text{Hence, } x = kt \quad (4)$$

$$\text{or } k = \frac{x}{t} \quad (5)$$

This is the general equation for zero-order reaction.

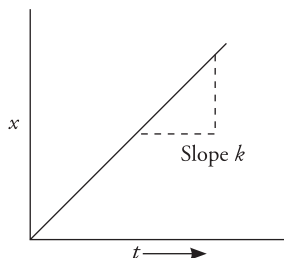


Figure 13.4 Zero-order plot

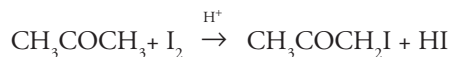
Unit of k

$$k = \text{conc time}^{-1} = \text{mol L}^{-1} \text{s}^{-1}.$$

The concentration of product increases linearly with time. The plot of x vs time (t) will be a straight line passing through the origin.

Examples include

- Photochemical combination of H_2 and Cl_2 over water (saturated with HCl) surface is a zero-order reaction.
- Thermal decomposition of HI on gold surface.
- The reaction between acetone and iodine is found to be of zero order with respect to iodine.



The observed rate law for this reaction is

$$-\frac{d[\text{I}_2]}{dt} = k[\text{H}_3\text{O}^+][\text{CH}_3\text{COCH}_3]$$

$[\text{I}_2]$ is not included in the differential rate law; hence, the rate of reaction is of zero order with respect to iodine concentration.

Solved Examples

- Q1. The rate constant of a zero-order reaction is 0.2 mol/L/h . What will be the initial concentration of the reactant if after half an hour its concentration is 0.05 mol/L .

Solution

For a zero-order reaction;

$$k = \frac{\Delta c}{\Delta t} = \frac{\text{Change in concentration}}{\text{time}}; k = 0.2 \text{ mol/L/h}, x = 0.05 \text{ mol}, a = ?$$

Substituting these values,

$$0.2 = \frac{a - 0.05}{1/2} \quad \text{or } 0.2 \times 1/2 = a - 0.05$$

$$a = 0.1 + 0.05 = 0.15 \text{ mol/L.}$$

Q2. Determine the order of a reaction and rate constant for the decomposition of ammonia on a tungsten wire at 856 °C. Data obtained in an experiment are given below

Total pressure p (torr)	228	250	273	318
Time t (s)	200	400	600	1000

Solution

$$\text{At } t = 400 \text{ s} \quad k = \frac{250 - 228}{400 - 200} = \frac{22}{200} = 0.11 \text{ torr/s}$$

$$\text{At } t = 600 \text{ s} \quad k = \frac{273 - 228}{600 - 200} = \frac{45}{400} = 0.1125 \text{ torr/s}$$

$$\text{At } t = 1000 \text{ s} \quad k = \frac{318 - 228}{1000 - 200} = \frac{90}{800} = 0.1125 \text{ torr/s}$$

The three values of k are consistent and the rate of change of pressure remains almost constant. Hence, it is a zero-order reaction.

$$\text{The specific reaction rates are } = \frac{0.11 + 0.1125 + 0.1125}{3} = 0.1117 \text{ torr/s}$$

Kinetics of first-order reactions

A reaction is said to be a first-order reaction if the reaction rate is determined by one concentration variable only.

Consider a general first-order reaction.



Differential rate equation for the reaction rate:

$$-\frac{d[A]}{dt} = k[A]$$

This means that if the concentration of the reactant is doubled the rate of reaction will double and if the concentration of reactant increases four times the rate of reaction also increases four times. To calculate the integrated rate equation let the initial concentration of reactant A in gram moles per liter be 'a'. Let 'x' g mol/L of A decompose into products in time t. Then the concentration of A after time 't' is (a - x) and hence the rate of reaction at time t is

$$\frac{dx}{dt} \propto (a - x) \quad \text{or} \quad \frac{dx}{dt} = k_1 (a - x) \quad (1)$$

$\frac{dx}{dt}$ is the rate of formation of products. k_1 = first-order rate constant

Separating the variables and integrating

$$\int \frac{dx}{a-x} = \int k_1 dt \quad \therefore \left[\int \frac{dx}{a-x} = -\ln(a-x) \right]$$

$$-\log_e(a-x) = k_1 t + I \quad (2)$$

I = integration constant.

$$\text{At } t = 0, \quad x = 0 \quad I = -\log_e a \quad (3)$$

Placing the value of I in Eq. (2)

$$-\log_e(a-x) = k_1 t - \log_e a$$

$$\text{or, } \log_e a - \log_e(a-x) = k_1 t$$

$$\text{or } k_1 = \frac{1}{t} \log_e \frac{a}{a-x}$$

$$\text{or } k_1 = \frac{2.303}{t} \log_{10} \frac{a}{a-x} \quad (4)$$

Equation (4) is called the integrated equation or kinetic equation for first-order reaction.

Unit of k

The quantity $\frac{a}{a-x}$ is dimensionless; hence, the unit of k is time^{-1}

If $\log_e(a-x)$ is plotted against time t , a straight line is obtained whose slope is equal to $-k_1/2.303$ from which the value of k_1 can be evaluated.

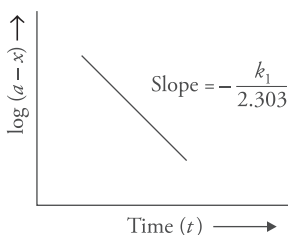


Figure 13.5 Plot of a first-order reaction

Examples of first-order reaction**1. Inversion of cane sugar**

Sugar in aqueous solution hydrolyses to give glucose and fructose:



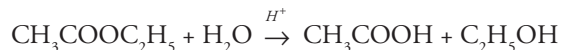
The reaction follows first-order kinetics as water is present in excess (pseudo-unimolecular reaction). The reaction is followed by measuring the optical rotation by means of a polarimeter. Sucrose rotates the plane of polarised light to the right; however, the resulting mixture rotates it to the left. If r_0 , r_t and r_∞ are the angles of rotation at the beginning ($t = 0$), at time t and at the end of the reaction, then the initial concentration of sucrose is proportional to $r_0 - r_\infty$, and the amount in time t is proportional to $r_0 - r_t$.

$$a - x = [(r_0 - r_\infty) - (r_t - r_\infty)] = (r_0 - r_t).$$

$$\text{Therefore, } k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

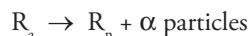
2. Hydrolysis of ester

Hydrolysis of ester when large excess of water is present follows first-order kinetics.



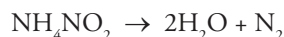
Again it is a pseudo-unimolecular reaction. The progress of the reaction is determined by titrating a given volume of the reaction mixture against standard alkali at definite time intervals. This gives the amount of CH_3COOH formed during the reaction. The final reading is taken after 24 hours. Suppose the titre value at the start, at time t and after infinite time (i.e., completion of the reaction) are V_0 , V_t and V_∞ , then $a = V_\infty - V_0$, $x = V_t - V_0$ and $a - x = V_\infty - V_t$.

$$\text{Therefore, } k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

3. Radioactive decay The disintegration of all radioactive substances follows first-order kinetics.

The velocity of disintegration is studied by recording the number of counts per second by a GM counter.

$$k = \frac{2.303}{t} \log \frac{R_0}{R_t} \quad \text{where } R_0 = \text{initial activity, } R_t = \text{final activity}$$

4. Decomposition of ammonium nitrite

The progress of the reaction is followed by collecting N_2 gas in a gas burette at different time intervals. The volume of the nitrogen at any time t corresponds to the amount of ammonium nitrite decomposed at that time (i.e., x). The amount of ammonium nitrite taken initially (i.e., a) is equal to the total volume of nitrogen collected when the reaction is completed.

If

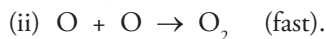
V_∞ = volume of nitrogen gas collected when reaction is completed and

V_t = volume of nitrogen collected at any time t then

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

5. Decomposition of N_2O_5

The reaction is of first order and proceeds in two steps.



The rate of reaction is determined by step (i) because it is the slow step in the reaction. The progress of the reaction is followed by measuring the volume of O_2 evolved. If

V_t = volume of O_2 evolved at time t and

V_∞ = volume of O_2 evolved when the reaction is completed then:

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

6. Decomposition of H_2O_2 This reaction also proceeds in two steps



The first step being the slow step is the rate-determining step. The reaction is followed by withdrawing equal volumes of H_2O_2 at different time intervals and then titrating with standard $KMnO_4$ solution. The value of $KMnO_4$ used at time t corresponds to the concentration of unreacted H_2O_2 at that time, that is $(a - x)$.

The volume of $KMnO_4$ at the start of the reaction is V_0 , then $V_0 = a$ and the value at time t is V_t then $V_t = (a - x)$ at that particular time.

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Numerical problems

1. If the rate constant for a first-order reaction is $3 \times 10^{-10} \text{ s}^{-1}$ and the concentration of the reactant is 1.5 M, find the rate of the reaction.

Solution

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

$$\text{Given } k = 3 \times 10^{-10} \text{ s}^{-1}, [A] = 1.5 \text{ M}$$

$$\text{Rate} = 3 \times 10^{-10} \times 1.5 = 4.5 \times 10^{-10} \text{ mol s}^{-1}.$$

2. The optical rotation of cane sugar in 0.5 N HCl at 35 °C and at various intervals is given below. Show that the reaction is a first-order reaction:

Time (min)	0	20	40	80	∞
Rotation (degree)	+ 32.4	+ 25.5	+ 19.6	+ 10.3	-14.1.

Solution

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{Here } a \propto r_0 - r_\infty = 32.4 - (-14.1) = 46.5$$

$$\text{And } a-x \propto r_t - r_\infty$$

t (min)	$r_t - r_\infty$	$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$
20	$25.5 - (-14.1) = 39.6$	$k = \frac{2.303}{20} \log \frac{46.5}{39.6} = 0.008039 / \text{min}$
40	$19.6 - (-14.1) = 33.7$	$k = \frac{2.303}{40} \log \frac{46.5}{33.7} = 0.008050 / \text{min}$
80	$10.3 - (-14.1) = 24.4$	$k = \frac{2.303}{80} \log \frac{46.5}{24.4} = 0.008062 / \text{min}$

A constant value of k is obtained which shows that the reaction is of first order. The average value of k is 0.0080503/min. $\text{Avg} = \frac{0.008039 + 0.008050 + 0.008062}{3} = 0.0080503$

3. The following observations were made during the hydrolysis of methyl acetate at 25 °C, using 0.05 N HCl as catalyst.

t (sec)	0	75	119	183	∞
Volume of alkali used (mL)	9.62	12.10	13.10	14.75	21.05

Show that the reaction is of first order.

Solution Here

$$a \propto V_{\infty} - V_0 = 21.05 - 9.62 = 11.43 \text{ mL}$$

$$(a - x) \propto V_{\infty} - V_t$$

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Time (s)	$V_{\infty} - V_t$	$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$
75	$21.05 - 12.10 = 8.95$	$k = \frac{2.303}{75} \log \frac{11.43}{8.95} = 0.003259 \text{ s}^{-1}$
119	$21.05 - 13.10 = 7.95$	$k = \frac{2.303}{119} \log \frac{11.43}{7.95} = 0.003051 \text{ s}^{-1}$
183	$21.05 - 14.75 = 6.30$	$k = \frac{2.303}{183} \log \frac{11.43}{6.3} = 0.003254 \text{ s}^{-1}$

As the value of k obtained is almost constant, the reaction is of first order. Average value of $k = 0.003188 \text{ s}^{-1}$.

4. The following results were obtained for the decomposition of nitrogen peroxide in an inert solvent.

t (s)	0	300	600	900	∞
Volume of O_2 evolved (cm^3)	0	3.42	6.30	8.95	34.75

Prove that the reaction is of first order and find the rate constant.

Solution

The reaction will be of first order if it obeys the equation.

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

As the reaction is followed by collecting O_2 at different time intervals, hence

$V_{\infty} = a$, $V_{\infty} - V_t = a - x$, $V_t \propto x$. The above equation becomes

$$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$$

Time (s)	$k = \frac{2.303}{t} \log \frac{V_{\infty}}{V_{\infty} - V_t}$
300	$k = \frac{2.303}{300} \log \frac{34.75}{34.75 - 3.42} = 0.000345 \text{ s}^{-1}$
600	$k = \frac{2.303}{600} \log \frac{34.75}{34.75 - 6.30} = 0.000333 \text{ s}^{-1}$
900	$k = \frac{2.303}{900} \log \frac{34.75}{34.75 - 8.95} = 0.000331 \text{ s}^{-1}$

As the value of k is almost constant, the reaction is of first order. The average value of rate constant $\frac{0.000345 + 0.000333 + 0.000331}{3} = 0.000336 \text{ s}^{-1}$

5. The catalysed decomposition of hydrogen peroxide in aqueous solution, which is of the first order, is followed by titrating equal volumes of samples of the solution with potassium permanganate at stated time as follows

t (min)	0	5	15	25	45
Volume of KMnO_4 used	37.0	29.8	19.6	12.3	5.0

Calculate the rate constant.

Solution

For a first-order reaction $k = \frac{2.303}{t} \log \frac{a}{a-x}$. The volume of KMnO_4 used gives the amount of unused H_2O_2 in the reaction mixture; hence,

$$V_0 \propto a \quad V_t \propto a - x$$

Substituting the values

t (min)	$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$
5	$k = \frac{2.303}{5} \log \frac{37.0}{29.8} = 4.329 \times 10^{-2} \text{ min}^{-1}$
15	$k = \frac{2.303}{15} \log \frac{37.0}{19.6} = 4.236 \times 10^{-2} \text{ min}^{-1}$

25	$k = \frac{2.303}{25} \log \frac{37.0}{12.3} = 4.407 \times 10^{-2} \text{ min}^{-1}$
45	$k = \frac{2.303}{45} \log \frac{37.0}{5.0} = 4.447 \times 10^{-2} \text{ min}^{-1}$

As the value of k is nearly constant, the reaction follows first-order kinetics. The average value of rate constant is $4.355 \times 10^{-2} \text{ min}^{-1}$.

6. The decomposition of N_2O_5 (g) is a first-order reaction. If the initial concentration of N_2O_5 (g) is 0.03 mol/L , what will be its concentration after 30 min, if the rate constant of the reaction is $1.35 \times 10^{-4} \text{ s}^{-1}$.

Solution

$$k = 1.35 \times 10^{-4} \text{ s}^{-1} \quad a = 0.03 \text{ mol/L} \quad t = 30 \text{ min} = 1800 \text{ s} \quad (a - x) = ?$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$1.35 \times 10^{-4} = \frac{2.303}{1800} \log \frac{0.03}{0.03-x}$$

$$\text{or} \quad \log \frac{0.03}{0.03-x} = \frac{1.35 \times 10^{-4} \times 1800}{2.303} = 0.1055$$

$$\text{or} \quad \frac{0.03}{0.03-x} = \text{Antilog } 0.1055 = 1.274$$

$$\text{or } x = 0.00645$$

Hence, concentration of N_2O_5 after 30 min = $(a - x)$

$$= 0.03 - 0.00645 = 0.02355 \text{ mol L}^{-1}.$$

7. A first-order reaction is 20% completed in 10 min. Calculate the time taken for the reaction to go to 80% completion?

Solution

$$\text{If } a = 1, \text{ then } x_1 = 0.20 \quad t_1 = 10 \text{ min}$$

$$x_2 = 0.80 \quad t_2 = ?$$

For the first-order reaction

$$k = \frac{2.303}{t_1} \log \frac{a}{a - x_1} \quad (1)$$

$$k = \frac{2.303}{t_2} \log \frac{a}{a - x_2} \quad (2)$$

Equating Eq. (1) and (2), we get

$$\frac{2.303}{t_1} \log \frac{a}{a - x_1} = \frac{2.303}{t_2} \log \frac{a}{a - x_2}$$

$$\frac{2.303}{10} \log \frac{1}{1 - 0.2} = \frac{2.303}{t_2} \log \frac{1}{1 - 0.8}$$

$$\frac{2.303}{10} \log \frac{1}{0.8} = \frac{2.303}{t_2} \log \frac{1}{0.2}$$

$$\frac{2.303}{10} \times 0.0969 = \frac{2.303}{t_2} \times 0.699$$

$$t_2 = \frac{0.699 \times 10}{0.0969} = 72.136 \text{ min}$$

$$t_2 = 72.136 \text{ min.}$$

8. What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the products in 200 min?

Solution

$$\text{Rate constant } k = 10^{-3} \text{ min}^{-1}$$

$$\text{Initial rate} = k[A]$$

$$= (10^{-3} \text{ min}^{-1}) \times (0.2 \text{ mol dm}^{-3})$$

$$= 2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}.$$

The integrated equation for first-order reaction is

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\text{or } \log \frac{a}{a-x} = \frac{kt}{2.303}$$

$$t = 200 \text{ min} \quad k = 10^{-3} \text{ min}^{-1} \quad \text{so that}$$

$$\log \frac{a}{a-x} = \frac{10^{-3} \times 200}{2.303} = 8.68 \times 10^{-2} \quad (2)$$

$$\text{or } \frac{a}{a-x} = 1.22 \quad (\text{antilog } 8.68 \times 10^{-2} = 1.22)$$

$$\text{or } a = 1.22a - 1.22x$$

$$\text{or } 1.22x = 1.22a - a = 0.22a$$

$$x = \frac{0.22a}{1.22} = 0.18a$$

$$\% \text{ conversion} = \frac{0.18a \times 100}{a} = 18\%$$

$$\text{Ans} = 18\%$$

Practice problems

1. The rate constant for a first-order reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + 1/2 \text{O}_2$ is $6.2 \times 10^{-6} \text{ s}^{-1}$. If the initial concentration of N_2O_5 is 15 mol L^{-1} , calculate the initial rate of the reaction.

$$[\text{Ans} \quad \text{Rate of reaction} = 9.3 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}]$$

2. To measure the rate of decomposition of hydrogen peroxide at a particular temperature its solution is titrated with acidic KMnO_4 solution. The results obtained are as follows:

Time t (min)	0	10	20
Vol of KMnO_4 used	22.8	13.8	8.3

Show that the reaction is of first order and calculate the rate constant.

$$[\text{Ans} \quad k = 0.05037 \text{ min}^{-1}]$$

3. A reaction is first order with respect to reactant X. It has a rate constant of 8 min^{-1} . If the initial concentration of $[\text{X}] = 7.0 \text{ mol L}^{-1}$, find the time required by $[\text{X}]$ to reach the value of 0.07 mol L^{-1} .

$$[\text{Ans} \quad t = 0.5757 \text{ min}]$$

4. The following data were obtained on the hydrolysis of methyl acetate at 25 °C in 0.35 N hydrochloric acid. Establish that the reaction follows first-order kinetics. Calculate the rate constant.

t (s)	0	4500	7140	∞
mL of alkali used	24.36	29.32	31.72	47.15

[Ans $k = 5.45915 \times 10^{-5} \text{ s}^{-1}$]

5. The optical rotation of sucrose in 0.9 M HCl at different time intervals is given in the following table. Show that the reaction is of first order. Calculate the rate constant.

Time (min)	0	6.18	18.00	27.05	∞
Rotation (degrees)	+24.09	+21.4	+17.7	+15.0	-10.74

[Ans $k = 0.011817 \text{ min}^{-1}$]

6. The following results were obtained in the decomposition of N_2O_4 in CCl_4 at 44 °C:

t (s)	1200	1800	2400	∞
x (mL)	11.40	15.53	18.90	34.75

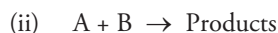
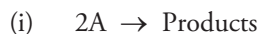
where x denotes the volume of oxygen evolved in t seconds. Show that the reaction is of first order.

[Ans A fairly constant value of k is obtained using the first-order equation. This shows that it is a first-order reaction.]

Kinetics of second-order reaction

When the reaction rate depends on the concentration of two reactants or the square of the concentration of a single reactant, it is said to be a second-order reaction.

It can be represented as follows



Case 1 Let us consider the first case



The differential rate equation

$$-\frac{d[\text{A}]}{dt} = k_2[\text{A}]^2$$

k_2 is the second-order rate constant. The above equation implies that if the concentration of the reactant is doubled the rate of the reaction quadruples and if the concentration of reactant increases by a factor of four then the rate of reaction increases by 4^2 , that is, it increases sixteen times. To calculate the integrated rate equation for a second-order reaction let us suppose 'a' is the initial

concentration of A in g mol/L. Let x g mol/L decompose in time t . According to the law of mass action, the rate of such a reaction is given by

$$\frac{dx}{dt} \propto (a-x)^2 \quad \text{or,} \quad \frac{dx}{dt} = k_2 (a-x)^2 \quad (1)$$

Separating the variables and integrating

$$\int \frac{dx}{(a-x)^2} = \int k_2 dt$$

$$\frac{1}{a-x} = k_2 t + I \quad (2)$$

where I is the integration constant. When $t = 0$ $x = 0$, Eq. (2) becomes

$$I = \frac{1}{a} \quad (3)$$

Substituting the value of I in Eq. (2), we have

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

$$\text{or } k_2 t = \frac{1}{a-x} - \frac{1}{a}$$

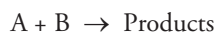
$$k_2 = \frac{1}{t} \left[\frac{1}{a-x} - \frac{1}{a} \right]$$

$$k_2 = \frac{1}{t} \left[\frac{a-(a-x)}{a(a-x)} \right] = \frac{1}{at} \left[\frac{x}{(a-x)} \right]$$

$$k_2 = \frac{x}{at(a-x)} \quad (4)$$

Equation (4) is known as the integrated rate equation for second-order reaction.

Case II Let us consider the second case.



Differential rate equation

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2 [A][B]$$

If a and b are the initial concentrations in g mol/L of A and B, respectively, and x g mol/L decomposes in time t , then

$$\frac{dx}{dt} \propto (a-x)(b-x)$$

$$\frac{dx}{dt} = k_2 (a - x)(b - x) \quad (1)$$

where k_2 is the rate constant for the second-order reaction. On separating the variables,

$$\frac{dx}{(a - x)(b - x)} = k_2 dt \quad (2)$$

Using partial fractions, Eq. (2) may be written as

$$\frac{1}{(a - b)} \left[\frac{1}{(b - x)} - \frac{1}{(a - x)} \right] dx = k_2 dt$$

$$\text{or } \frac{1}{(a - b)} \left[\frac{dx}{(b - x)} - \frac{dx}{(a - x)} \right] = k_2 dt$$

On integrating the above equation, we obtain

$$\frac{1}{(a - b)} [-\ln(b - x) + \ln(a - x)] = k_2 t + I \quad (3)$$

I is the integration constant. When $t = 0$ and $x = 0$, Eq. (3) reduces to

$$\frac{1}{(a - b)} [-\ln(b) + \ln(a)] = I \quad (4)$$

Substituting the value of I in Eq. (3)

$$\frac{1}{(a - b)} [-\ln(b - x) + \ln(a - x)] = k_2 t + \frac{1}{(a - b)} [-\ln(b) + \ln(a)]$$

$$\text{or } \frac{1}{(a - b)} \ln \frac{(a - x)}{(b - x)} - \frac{1}{(a - b)} \ln \frac{a}{b} = k_2 t$$

$$\text{or } \frac{1}{(a - b)} \left[\ln \frac{(a - x)b}{(b - x)a} \right] = k_2 t$$

$$k_2 t = \frac{2.303}{(a - b)} \log_{10} \frac{b(a - x)}{a(b - x)}$$

$$k_2 = \frac{2.303}{(a - b)t} \log_{10} \frac{b(a - x)}{a(b - x)} \quad (5)$$

Equation (5) is known as the integrated rate equation or the kinetic equation for second-order reaction.

Unit of k

Consider the rate equation

$$k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

$$k_2 = \frac{1}{s} \cdot \frac{\text{conc}}{\text{conc} \times \text{conc}}$$

$$k_2 = \text{conc}^{-1} \text{s}^{-1}$$

So the unit of second-order rate constant is

$$k_2 = (\text{mol/L})^{-1} \text{s}^{-1} = \text{L mol}^{-1} \text{s}^{-1}$$

Examples of second-order reaction

In gas phase

- (i) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
- (ii) $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$
- (iii) $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
- (iv) $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$.

In liquid phase

- (i) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
- (ii) $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$
- (iii) $\text{NH}_4\text{CNO} \rightleftharpoons \text{NH}_2\text{CONH}_2$
Ammonium cyanate Urea
- (iv) $2\text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{CHOHCOC}_6\text{H}_5$
Benzaldehyde Benzoin

For a second-order reaction,

$$k_2 = \frac{x}{at(a-x)}$$

This equation can be written as

$$\frac{1}{(a-x)} = k_2 t + \frac{1}{a}$$

$$y = mx + c$$

This is the equation of a straight line where $y = \frac{1}{(a-x)}$, and hence the plot of $\frac{1}{(a-x)}$ against t will be a straight line as shown in Figure 13.6. The rate constant $k = \text{slope}$.

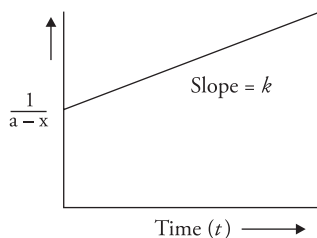
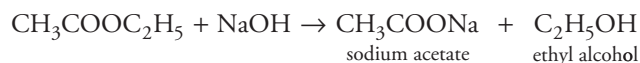


Figure 13.6 Plot of a second-order reaction

Saponification (alkaline hydrolysis) of esters:

It is the reaction of esters with NaOH



Equal volumes of $\text{CH}_3\text{COOC}_2\text{H}_5$ and NaOH are used for the reaction. The reaction is followed by studying the amount of NaOH at a given time and this is done by withdrawing a definite amount of reaction mixture and titrating it with standard acid. The same volume of reaction mixture is withdrawn at different time intervals.

The amount of NaOH at $t=0$ is proportional to the volume of standard acid (V_o) used at the beginning of the reaction.

$$V_o \propto a$$

Volume of standard acid used at time t , that is, V_t is proportional to the concentration of NaOH at time t

$$V_t \propto a - x$$

$$\text{Hence } [a - (a - x)] \text{ or } x = V_o - V_t$$

Substituting these values in the second-order rate equation we get

$$k = \frac{x}{at(a-x)} = \frac{1}{t} \cdot \frac{V_o - V_t}{V_o V_t}$$

Solved Examples

1. A second-order reaction where $a = b$ is 20% completed in 500 s. Find the time taken for 80% completion of the reaction.

Solution

$$\text{If } a = 1 \quad x_1 = 0.2, \quad t_1 = 500 \text{ s}$$

$$x_2 = 0.8, \quad t_2 = ?$$

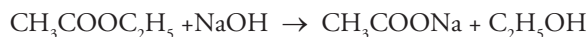
$$k_2 = \frac{x_1}{at_1(a-x_1)} = \frac{x_2}{at_2(a-x_2)}$$

$$\frac{0.2}{1 \times 500(1-0.2)} = \frac{0.8}{1 \times t_2(1-0.8)}$$

$$\frac{0.2}{400} = \frac{0.8}{0.2 \times t_2}$$

$$\text{or } t_2 = \frac{0.8 \times 400}{0.2 \times 0.2} = 8000 \text{ s}$$

2. In the saponification of ethyl acetate by NaOH, the following data were obtained:



Initial concentration of ethyl acetate = caustic soda = 10 mol/L

Time (min) 0 15 25 35 55

$a-x$	10	4.9	3.6	2.9	2.1
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Show that it is a second-order reaction.

Solution

Here $a = 10$

t (min)	$a - x$	$x = [a - (a - x)]$	$k_2 = \frac{x}{at(a - x)}$
0	10(= a)	0	
15	4.9	5.1	$k_2 = \frac{5.1}{15 \times 10 \times (4.9)} = 0.0069 \text{ L mol}^{-1} \text{ min}^{-1}$
25	3.6	6.4	$k_2 = \frac{6.4}{10 \times 25 \times (3.6)} = 0.0071 \text{ L mol}^{-1} \text{ min}^{-1}$
35	2.9	7.1	$k_2 = \frac{7.1}{35 \times 10 \times (2.9)} = 0.00699 \text{ L mol}^{-1} \text{ min}^{-1}$
55	2.1	7.9	$k_2 = \frac{7.9}{55 \times 10 \times (2.1)} = 0.0068 \text{ L mol}^{-1} \text{ min}^{-1}$

The value of k_2 is almost constant; hence, it is a second-order reaction.

3. In a second-order reaction, the initial concentration of reactants is 0.1 mol L^{-1} . The reaction is found to be 20% complete in 40 min. Calculate

(i) rate constant

(ii) half-life period

(iii) time taken to complete 75% of the reaction

Solution

Here,

$$a = 0.1 \text{ mol L}^{-1} \quad x = 0.2 \times a = 0.2 \times 0.1 = 0.02 \text{ mol L}^{-1}$$

$$t = 40 \text{ min} \quad (a - x) = 0.1 - 0.02 = 0.08 \text{ mol L}^{-1}$$

- (i) For a second-order reaction

$$k_2 = \frac{x}{at(a-x)} = \frac{0.02}{0.1 \times 40 \times 0.08} = 0.0625 \text{ L mol}^{-1} \text{ min}^{-1}$$

- (ii)
- $k_2 = 0.0625 \text{ L mol}^{-1} \text{ min}^{-1}$
- $t_{1/2} = ?$

$$\text{Half-life } t_{1/2} = \frac{1}{k_2 a} = \frac{1}{0.0625 \times 0.1} = 160 \text{ min}$$

- (iii)
- $x' = 0.75a = 0.75 \times 0.1 = 0.075 \text{ mol L}^{-1}$

$$k = 0.0625 \text{ L mol}^{-1} \text{ min}^{-1} \quad t' = ?$$

$$(a - x') = (0.1 - 0.075) = 0.025 \text{ mol L}^{-1}$$

$$\text{But } k = \frac{x'}{at'(a-x')}$$

$$t' = \frac{0.075}{0.1 \times 0.0625 \times 0.025} = 480 \text{ min or 8 h}$$

$$[\text{Ans } k = 0.0625 \text{ L mol}^{-1} \text{ min}^{-1} \quad t_{1/2} = 160 \text{ min} \quad t_{75\%} = 480 \text{ min}]$$

Practice Problems

1. Ethyl acetate was hydrolysed by NaOH. Equal concentration of NaOH and ethyl acetate was used for the hydrolysis reaction. 25 mL of the reaction mixture was titrated against standard acid at regular time intervals. From the data given below, establish that it is a second-order reaction:

t (min)	0	5	15	25	35
mL of acid used	16.00	10.24	6.13	4.32	3.41

[Ans A fairly constant value of k shows that it is a second-order reaction. Average value of $k = 0.006773 \text{ L mol}^{-1} \text{ min}^{-1}$]

2. Ethyl nitro benzoate was hydrolysed by aqueous sodium hydroxide at 25 °C. The progress of the reaction was followed by titrating the hydroxide against standard acid at different intervals of time. From the data given below, show that the reaction is of second order.

t (min)	0	95	140	222	334	805	1384
mL of acid used	10	9.3	9.0	8.5	7.9	6.1	4.8

[Ans A fairly constant value of k shows that it is a second-order reaction. Average value of $k = 7.9923 \times 10^{-5} \text{ L mol}^{-1}\text{min}^{-1}$]

Kinetics of n^{th} -order reaction

Consider a reaction of n^{th} order that takes place as follows:



In this reaction, all the reactants are of the same initial concentration. Suppose the initial concentration of A is 'a' g mol/L. Let x g mol/L decompose in time t . Then the concentration of A at time t will be $(a - x)$. According to the law of mass action, the rate of n^{th} order is given by

$\frac{dx}{dt} \propto (a - x)^n$ or $\frac{dx}{dt} = k_n(a - x)^n$ where k_n is the rate constant of the n^{th} order reaction. Separating the variables and integrating

$$\int \frac{dx}{(a - x)^n} = \int k_n dt$$

$$\frac{1}{(n-1)(a - x)^{n-1}} = k_n t + I \quad (1)$$

I = Integration constant. When $t = 0$ and $x = 0$, Eq. (1) becomes

$$I = \frac{1}{(n-1)(a)^{n-1}} \quad (2)$$

Substituting the value of I in Eq. (1), we get

$$\frac{1}{(n-1)(a - x)^{n-1}} = k_n t + \frac{1}{(n-1)(a)^{n-1}}$$

$$k_n t = \left[\frac{1}{(n-1)(a - x)^{n-1}} - \frac{1}{(n-1)(a)^{n-1}} \right]$$

$$k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

This is known as the integrated rate expression for n^{th} -order reaction.

13.10 Half-life of a Reaction

The time in which the concentration of the reactant reduces to half of its original value is termed as the half-life of a reaction. It is generally denoted as $t_{1/2}$.

(i) Half-life of a zero-order reaction

The rate equation for zero-order reaction

$$k_0 = \frac{x}{t} \quad \text{when } t = t_{1/2} \quad x = a/2 \quad (a = \text{initial concentration of the reactants})$$

$$t_{1/2} = \frac{a}{2k_0} \quad \text{or} \quad t_{1/2} \propto a$$

Thus in a zero-order reaction the half-life is directly proportional to the initial concentration of the reactant. In other words, half-life decreases as the concentration decreases or the half-life decreases as the reaction proceeds.

(ii) Half-life of first-order reaction

For a first-order reaction

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

When $t = t_{1/2}$ $x = a/2$, the above equation becomes

$$k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{a-a/2}$$

$$k_1 = \frac{2.303}{t_{1/2}} \log 2 = \frac{2.303 \times 1.414}{t_{1/2}}$$

$$t_{1/2} = \frac{0.693}{k_1}$$

Thus for a first-order reaction, the half-life does not depend on the initial concentration of the reactants, hence it remains constant throughout the reaction.

(iii) Half-life of second-order reaction

For a second-order reaction

$$k_2 = \frac{x}{at(a-x)}$$

When $t = t_{1/2}$ $x = a/2$, the above equation becomes

$$k_2 = \frac{a/2}{at_{1/2}(a-a/2)} = \frac{a/2}{at_{1/2} \times a/2}$$

$$k_2 = \frac{1}{at_{1/2}} \quad \text{or} \quad t_{1/2} = \frac{1}{k_2 a}$$

Thus, for a second-order reaction the half-life of the reaction varies inversely with the initial concentration. In other words, half-life increases as concentration of the reactant decreases or as the reaction proceeds forward.

(iv) **Half-life of n^{th} -order reaction**

$$k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

When $t = t_{1/2}$ $x = a/2$, the above equation becomes

$$\begin{aligned} k_n &= \frac{1}{(n-1)t_{1/2}} \left[\frac{1}{(a-a/2)^{n-1}} - \frac{1}{a^{n-1}} \right] \\ &= \frac{1}{(n-1)t_{1/2}} \left[\frac{2^{n-1}}{a^{n-1}} - \frac{1}{a^{n-1}} \right] \end{aligned}$$

$$k_n = \frac{1}{(n-1)t_{1/2}a^{n-1}} (2^{n-1} - 1)$$

$$t_{1/2} = \frac{1}{(n-1)k_n a^{n-1}} (2^{n-1} - 1) \quad \text{or} \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

Thus, the time required to complete half reaction of n^{th} -order reaction is inversely proportional to the initial concentration raised to the power that is one less than the order of the reaction.

Table 13.3 Summary of the relationship of zero, first, second and n^{th} -order reactions

Order of the reaction	Differential rate law	Integrated rate equation	Half-life	Unit of k
Zero	$-\frac{d[A]}{dt} = k[A]^0$	$k_0 = \frac{x}{t}$ $k_0 = \frac{\Delta c}{\Delta t} = \frac{c_0 - c}{t_2 - t_1}$	$t_{1/2} = \frac{a}{2k_0}$	$\text{mol L}^{-1} \text{s}^{-1}$
First	$-\frac{d[A]}{dt} = k_1[A]$	$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$	$t_{1/2} = \frac{0.693}{k_1}$	time^{-1} or s^{-1} , k is independent of initial concentration

Second	$-\frac{d[A]}{dt} = k_2[A]^2$	$k_2 = \frac{x}{at(a-x)}$	$t_{1/2} = \frac{1}{k_2 a}$	$L \text{ mol}^{-1} \text{ s}^{-1}$
n^{th}	$-\frac{d[A]}{dt} = k_n[A]^n$	$k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$	$t_{1/2} = \frac{1}{(n-1)k_n a^{n-1}} (2^{n-1} - 1)$	$L^{n-1} \text{ mol}^{1-n} \text{ time}^{-1}$ or $(\text{mol/L})^{1-n} \text{ time}^{-1}$

Solved Examples

1. If the initial concentration of a reactant is changed from 1.0 to 2.0 mol /L, the time required for the reaction to be half completed is found to change from 100 to 50 s. Calculate the time taken for the concentration to be reduced to 30% of the initial value.

Solution

Half-life is related to initial concentration as follows:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

Here $t_1 = 100 \text{ s}$; $t_2 = 50 \text{ s}$; $a_1 = 1.0 \text{ mol/L}$ and $a_2 = 2.0 \text{ mol/L}$

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1} = \frac{100}{50} = \left(\frac{2}{1} \right)^{n-1} \quad \text{or} \quad 2 = (2)^{n-1}$$

$$\text{or} \quad n-1=1 \quad \text{or} \quad n=2$$

That is, the reaction is of second order.

For a second-order reaction

$$k = \frac{1}{t_{1/2} a} = \frac{1}{100 \text{ s} \times 1.0 \text{ mol L}^{-1}} = \frac{1}{100 \text{ mol L}^{-1} \text{ s}}$$

$$\text{now } a = 1; \quad a - x = 0.3 \quad x = 0.7 \quad t = ?$$

$$\text{also } t = \frac{x}{ak(a-x)} = \frac{0.7 \text{ mol L}^{-1} \times 100 \text{ mol L}^{-1} \text{ s}^{-1}}{1.0 \text{ mol L}^{-1} \text{ s} \times 0.3 \text{ mol L}^{-1}} = 233.33 \text{ s}$$

2. For a first-order reaction prove that the time required for 99.9% completion of the reaction is ten times the time required for 50% completion of the reaction, that is, $\frac{t_{0.999}}{t_{1/2}} = 10$

Solution For a first-order reaction

$$(i) \quad t_{1/2} = \frac{0.693}{k} \quad (1)$$

(ii) for 99.9% completion of the reaction

If $a = 1$; $x = 0.999$ or $a - x = 0.001$

$$\begin{aligned}
 t_{0.999} &= \frac{2.303}{k} \log \frac{1}{0.001} \\
 &= \frac{2.303}{k} \log 1000 \\
 &= \frac{2.303 \times 3}{k} = \frac{6.909}{k}
 \end{aligned} \tag{2}$$

Dividing equation 2 by 1 we get

$$\frac{t_{0.999}}{t_{1/2}} = \frac{6.909}{k} \times \frac{k}{0.693} \approx 10$$

hence, $t_{0.999} = 10 t_{1/2}$ Hence proved

3. The specific rate constant of a first-order reaction is (a) 200 s^{-1} , (b) 4 min^{-1} and (c) 5 year^{-1} . Calculate the half-life of the reaction in each case.

Solution

For a first-order reaction

$$t_{1/2} = \frac{0.693}{k}$$

- (i) $k = 200 \text{ s}^{-1}$

$$t_{1/2} = \frac{0.693}{200} = 3.465 \times 10^{-3} \text{ s}$$

- (ii) $k = 4 \text{ min}^{-1}$

$$t_{1/2} = \frac{0.693}{4} = 0.1732 \text{ min}$$

- (iii) $k = 5 \text{ year}^{-1}$

$$t_{1/2} = \frac{0.693}{5} = 0.1386 \text{ year}$$

4. The thermal decomposition of a compound follows first-order kinetics. If 50% of the compound is decomposed in 120 min, in how much time will 90% of the compound decompose?

Solution

Let us first calculate the value of k

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{120} = 5.77 \times 10^{-3} \text{ min}^{-1}$$

Now for a first-order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$a = 1; \quad x = 0.9 \quad \text{or} \quad a - x = 1 - 0.9 = 0.1$$

$$\begin{aligned} t &= \frac{2.303}{5.77 \times 10^{-3}} \log \frac{1}{0.1} \\ &= \frac{2.303}{5.77 \times 10^{-3}} \log 10 = 399 \text{ min} \end{aligned}$$

5. A reaction follows second-order kinetics. The initial concentration of both the reactants is the same and half of the reactants are consumed in 60 min. If the specific reaction rate is $5.2 \times 10^{-3} \text{ mol}^{-1} \text{ L min}^{-1}$, find the initial concentration of the reactants?

Solution

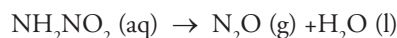
For a second-order reaction

$$\begin{aligned} t_{1/2} &= \frac{1}{k_2 a} \\ \text{or } a &= \frac{1}{t_{1/2} \cdot k_2} = \frac{1}{60 \times 5.2 \times 10^{-3}} = 3.2 \text{ mol L}^{-1} \end{aligned}$$

$$\text{initial concentration} = 3.2 \text{ mol L}^{-1}$$

Practice problems

- The decomposition of a substance follows first-order kinetics. Calculate the rate constant of the reaction if its half-life is 35 min. [Ans $k = 1.98 \times 10^{-2} \text{ min}^{-1}$]
- For a first-order reaction, prove that the time taken for three fourth completion of the reaction is double the time taken for half completion of the reaction, that is, $t_{3/4} / t_{1/2} = 2$.
- If the rate constant k for a first-order reaction is $5.48 \times 10^{-14} \text{ s}^{-1}$, find the time taken for two-third of the reaction to be completed. [Ans $t_{2/3} = 2.01 \times 10^{13} \text{ s}$]
- Decomposition of nitramide follows first-order kinetics. Its half-life is 3.2 h at 15°C .



If 7.1 g of NH_2NO_2 decomposes, calculate the time taken for 90% NH_2NO_2 to decompose.

$$[\text{Ans } k = 0.216 \text{ h}^{-1}; t = 10.66 \text{ h}]$$

13.11 Methods of Determining the Order of a Reaction

The various methods used for the determination of order of a reaction are as follows:

1. Integration method or hit and trial method

In this method, known quantities of the reactants are mixed in a reaction vessel and the progress of the reaction is noted by determining the amount of reactant consumed after different time intervals. The experimental data obtained are substituted in various equations for reactions of first order, second order, third order, and so on, turn by turn. The equation that gives the most concordant value of k gives the order of the reaction. Hence, the method involves the trial of one equation after another, till the correct one is found. Hence, it is also called hit and trial method.

2. **Fractional change method** As discussed earlier (Section 13.10), if the initial concentrations of all the reactants taking part in the chemical reaction are the same, then the time (t) required for the completion of a definite fraction of a n^{th} -order reaction is

$$t \propto \frac{1}{a^{n-1}}$$

Suppose we consider two experiments with initial concentrations a_1 and a_2 . Let t_1 and t_2 be the time to complete the same fraction of the reaction in the two experiments. Then

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

$$\frac{t_2}{t_1} = \frac{a_1^{n-1}}{a_2^{n-1}} \quad \text{or} \quad \frac{t_2}{t_1} = \left(\frac{a_1}{a_2} \right)^{n-1}$$

Taking logarithm of both the sides, we get

$$\log \frac{t_2}{t_1} = (n-1) \log \left(\frac{a_1}{a_2} \right)$$

$$\text{or} \quad (n-1)(\log a_1 - \log a_2) = \log t_2 - \log t_1$$

$$\text{or} \quad n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$$

By using the above equation, the order of the reaction can be calculated.

3. Graphical method

We know that for a first-order reaction

$$t = \frac{2.303}{k} \log a - \frac{2.303}{k} \log(a-x)$$

$$t \propto -\log(a - x) \quad (\text{for first-order reaction}).$$

For a second-order reaction

$$t = \frac{a}{ak(a-x)} = \frac{1}{k(a-x)} - \frac{1}{ka}$$

$$\text{or } t \propto \frac{1}{(a-x)} \quad (\text{for a second-order reaction}).$$

$$\text{In general, } t \propto \frac{1}{(a-x)^{n-1}} \quad (\text{for } n^{\text{th}}\text{-order reaction})$$

Now,

If graph of $\log(a-x)$ vs time(t) gives a straight line, the reaction is of first order.

If a plot of $1/(a-x)$ vs time t gives a straight line, the reaction is of second order and so on.

4. **Van't Hoff differential method**

It was suggested by Van't Hoff in 1884 that the rate of n^{th} -order reaction is

$$-\frac{dc}{dt} \propto c^n \quad \text{or} \quad -\frac{dc}{dt} = kc^n$$

where c is the concentration of reacting substance. Two experiments are conducted with initial reactant concentrations c_1 and c_2 , then

$$-\frac{dc_1}{dt} = kc_1^n \quad \text{and} \quad -\frac{dc_2}{dt} = kc_2^n$$

Taking log of both sides, we get

$$\log \left[-\frac{dc_1}{dt} \right] = \log k + n \log c_1 \tag{i}$$

$$\log \left[-\frac{dc_2}{dt} \right] = \log k + n \log c_2 \tag{ii}$$

Subtracting Eq. (ii) from Eq. (i) we get

$$\log \left[-\frac{dc_1}{dt} \right] - \log \left[-\frac{dc_2}{dt} \right] = n \log(c_1 - c_2)$$

$$n = \frac{\log \left[-\frac{dc_1}{dt} \right] - \log \left[-\frac{dc_2}{dt} \right]}{\log c_1 - \log c_2}$$

Thus, to calculate the value of n , we need to know the rates $-\frac{dc_1}{dt}$ and $-\frac{dc_2}{dt}$ at concentrations c_1 and c_2 , respectively. These values can be found out by plotting concentrations against time. The slope of the tangent at a given time interval gives the value of rate $-\frac{dc_1}{dt}$ and $-\frac{dc_2}{dt}$.

5. **Ostwald's isolation method** If the reaction involves more than one reactant, then Ostwald suggested the following method to determine the order of reaction. He suggested that all the reactants except one are to be taken in excess. The reactants taken in excess will have no effect on the reaction rate. Hence, the order as determined experimentally will be the order of reaction with respect to the reactant taken in smaller quantity. This reactant, which is taken in smaller quantity, is said to be the isolated reactant. The experiment is repeated by isolating each reactant one by one. The sum of the orders calculated by the isolated reactions gives the overall order of the reaction.

For example,



Rate of the reaction

$$\frac{dx}{dt} = kc_A^p \cdot c_B^q \cdot c_C^r$$

In the first experiment, the reactant A is isolated and the reactants B and C are taken in excess. The order of reaction as determined experimentally is the order with respect to A. Let the order be p . In the second experiment, A and C are taken in excess. In this case, the experimental result gives the order of the reaction with respect to the reactant B. Let it be q . Now order of the reaction with respect to C is found out by taking A and B in excess. Let it be r . Thus, the total order of the reaction will be $p + q + r$.

6. Initial rate method or the method of ratio variation

In this method, a series of experiments are carried out. The initial concentration of the reactants is varied in exact ratios (say doubled, tripled and so on). From the rate of reactions thus obtained, the order of the reaction can be determined. Let us consider two reactants A and B. To determine the order of the reaction a series of experiments are conducted in which the initial concentrations of A and B are varied. In the first experiment, the reaction rate is found out by taking a specific initial concentration of A and B. In the second experiment, the concentration of one of the reactants (say A) is kept constant and that of the other reactant (say B) is varied in exact ratio of the previous concentration, say it is doubled, tripled or quadrupled. The rate of reaction is found out experimentally, and from this the order of the reaction with respect to B can be calculated.

The experiment is repeated again. This time the concentration of A is varied in exact ratio and that of B is kept constant. The rate of the reaction thus obtained helps in calculating the order of the reaction with respect to A. The sum of the orders with respect to each of these reactants gives the total order of the reaction.

For a better understanding of the above method, let us consider the following example:



In the first experiment let the initial concentration of both A and B be 0.2 M and the initial rate of the reaction is say $1.2 \times 10^{-6} \text{ mol L}^{-1} \text{ min}^{-1}$. In the second experiment when the initial concentration of A is doubled (from 0.20 to 0.40 M) keeping concentration of B constant, the rate changes to 4.8×10^{-6} . In the third experiment, the concentration of B is tripled (from 0.20 to 0.60 M) keeping the concentration of A constant. The rate then becomes $1.44 \times 10^{-5} \text{ mol L}^{-1} \text{ min}^{-1}$. The order of the reaction can be calculated as given below.

Experiment	Initial concentration		Rate of reaction $\text{mol L}^{-1} \text{ min}^{-1}$
	A	B	
I	0.2	0.2	1.2×10^{-6}
II	0.4	0.2	4.8×10^{-6}
III	0.4	0.6	1.44×10^{-5}

The rate law may be written as

$$\text{Rate} = k[A]^p \cdot [B]^q$$

Comparing experiments I and II we get

$$(\text{Rate})_1 = k[0.2]^p \cdot [0.2]^q = 1.2 \times 10^{-6} \quad (1)$$

$$(\text{Rate})_2 = k[0.4]^p \cdot [0.2]^q = 4.8 \times 10^{-6} \quad (2)$$

Dividing Eq. (2) by (1)

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k[0.4]^p \cdot [0.2]^q}{k[0.2]^p \cdot [0.2]^q} = \frac{4.8 \times 10^{-6}}{1.2 \times 10^{-6}}$$

$$\text{or } (2)^p = 4 \quad \therefore p = 2. \quad \text{Thus, the order with respect to A is 2}$$

Comparing experiments II and III

$$(\text{Rate})_2 = k[0.4]^p \cdot [0.2]^q = 4.8 \times 10^{-6} \quad (3)$$

$$(\text{Rate})_3 = k[0.4]^p \cdot [0.6]^q = 1.44 \times 10^{-5} \quad (4)$$

Dividing Eq. (4) by (3) we get

$$\frac{k[0.4]^p \cdot [0.6]^q}{k[0.4]^p \cdot [0.2]^q} = \frac{1.44 \times 10^{-5}}{4.8 \times 10^{-6}}$$

$$\text{or } (3)^q = 3 \quad \therefore q = 1$$

$$\therefore \text{The order with respect to B is 1. Overall order of the reaction} = p + q = 2 + 1 = 3.$$

Practice Problems

1. In the saponification of ethyl acetate by NaOH at 283 K, y mL of 0.043 N HCl was required to neutralise 100 mL of the reaction mixture, t min after the commencement of the reaction

t (min)	0	4.89	10.37	28.18
y (mL)	61.95	50.59	42.40	29.35

Find out the order of the reaction and the velocity constant.

Solution

The order can be found out by integration or hit and trial method.

- (i) Let us first calculate the first-order rate constant $a=61.95$.

time (min)	$a - x$	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
4.89 min	50.59	$k = \frac{2.303}{4.89} \log \frac{61.95}{50.59} = 0.0414 \text{ min}^{-1}$
10.37 min	42.40	$k = \frac{2.303}{10.37} \log \frac{61.95}{42.40} = 0.0366 \text{ min}^{-1}$
28.18 min	29.35	$k = \frac{2.303}{28.18} \log \frac{61.95}{29.35} = 0.0265 \text{ min}^{-1}$

Since the values of k are not same, hence it is not a first-order reaction.

Now try for second order

Time	$a - x$	$x = a - (a - x)$	$k = \frac{x}{at(a-x)}$
4.89	50.59	61.95-50.59	$k = \frac{61.95 - 50.59}{61.95 \times 4.89 \times 50.59} = 0.000741 \text{ conc}^{-1} \text{ min}^{-1}$
10.37	42.40	61.95-42.40	$k = \frac{61.95 - 42.40}{61.95 \times 10.37 \times 42.40} = 0.000718 \text{ conc}^{-1} \text{ min}^{-1}$
28.18	29.35	61.95-29.35	$k = \frac{61.95 - 29.35}{61.95 \times 28.18 \times 29.35} = 0.000636 \text{ conc}^{-1} \text{ min}^{-1}$

As the values of k are almost identical, it is a second-order reaction.

- (ii) Velocity constant

$$k = \frac{0.000741 + 0.000718 + 0.000636}{3}$$

$$= 0.000698 \text{ conc}^{-1} \text{ min}^{-1} = 6.98 \times 10^{-4} \text{ conc}^{-1} \text{ min}^{-1}.$$

2. At a certain temperature, the half-life periods for the catalytic decomposition of ammonia were found to be as below:

Pressure (mm)	50	100	200
Half-life period	3.52	1.92	1.0

Find out the order of the reaction.

Solution

According to fractional change method,

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1} = \left(\frac{p_2}{p_1} \right)^{n-1}$$

- (i) Taking the first pair,

$$p_1 = 50, \quad p_2 = 100, \quad t_1 = 3.52, \quad t_2 = 1.92$$

$$\frac{3.52}{1.92} = \left(\frac{100}{50} \right)^{n-1}$$

Taking log of both side,

$$\begin{aligned} (n-1) \log 2 &= \log \frac{3.52}{1.92} \\ (n-1) \times 0.3010 &= 0.5465 - 0.2833 \\ n &= 0.8744 + 1 = 1.8744 \approx 2 \end{aligned}$$

- (ii) With the second pair,

$$p_1 = 100, \quad p_2 = 200, \quad t_1 = 1.92, \quad t_2 = 1.0$$

$$\frac{1.92}{1.0} = \left(\frac{200}{100} \right)^{n-1}$$

Taking log of both side,

$$\begin{aligned} (n-1) \log 2 &= \log 1.92 - \log 1 \\ (n-1) \times 0.3010 &= 0.2833 - 0 \\ n &= 1 + \frac{0.2833}{0.3010} = 1.9412 \approx 2 \end{aligned}$$

Hence, the reaction is of second order.

3. From the work of LT Reicher (1895) on the action of bromine on fumaric acid, the following data were obtained.

First Experiment		Second Experiment	
t(min)	Concentration	t (min)	Concentration.
0	8.87	0	3.81.
95	7.87	132	3.51.
Mean concentration = 8.37		Mean concentration = 3.66.	
$-\frac{dc_1}{dt} = 0.0106$		$-\frac{dc_2}{dt} = 0.00227$	

Find out the order of the reaction.

Solution

$$-\frac{dc_1}{dt} = 0.0106 \qquad -\frac{dc_2}{dt} = 0.00227$$

$$c_1 = 8.37 \qquad c_2 = 3.66$$

According to Van't Hoff differential method,

$$n = \frac{\log\left[-\frac{dc_1}{dt}\right] - \log\left[-\frac{dc_2}{dt}\right]}{\log c_1 - \log c_2}$$

$$n = \frac{\log[0.0106] - \log[0.00227]}{\log 8.37 - \log 3.66} = 1.87 \text{ or } n \approx 2$$

4. Consider a gaseous decomposition reaction $A \rightarrow \text{Products}$ at 500°C and at an initial pressure of 350 torr. The rate of the reaction was 1.07 torr/s when 5% of the decomposition was over and 0.76 torr/s, when 20% decomposition was over. Determine the order of the reaction.

Solution

According to van't Hoff differential method,

$$n = \frac{\log(\text{rate})_1 - \log(\text{rate})_2}{\log(\text{conc})_1 - \log(\text{conc})_2}$$

Given,

$$(\text{rate})_1 = 1.07 \text{ torr s}^{-1} \quad (\text{conc})_1 \text{ if } a = 1 \quad x_1 = 0.05 \quad a - x_1 = 0.95$$

similarly

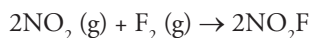
$$(\text{rate})_2 = 0.76 \text{ torr s}^{-1} \quad (\text{conc})_2 = a - x_2 = 1 - 0.2 = 0.80$$

Placing these values in the equation we get

$$n = \frac{\log 1.07 - \log 0.76}{\log 0.95 - \log 0.80} \approx 2$$

Hence the order of the reaction is 2

5. The following data were obtained for the reaction



Experiment No.	Initial concentration		Initial rate mol L ⁻¹ min ⁻¹
	[NO ₂]	[F ₂]	
1	0.20	0.05	6.0×10 ⁻³
2	0.40	0.05	1.2×10 ⁻²
3	0.80	0.10	4.8×10 ⁻²

Determine (i) the order of the reaction, (ii) rate law and (iii) rate of reaction when [NO₂]=0.5 mol L⁻¹.
[F₂] = 0.60 mol L⁻¹.

Solution

The initial rate expression may be written as

$$(\text{rate})_0 = k[\text{NO}_2]^p [\text{F}_2]^q \quad \text{eq(1)}$$

Comparing experiments (1) and (2) we get

$$(\text{rate})_1 = k[0.2]^p [0.05]^q = 6.0 \times 10^{-3} \quad (\text{i})$$

$$(\text{rate})_2 = k[0.4]^p [0.05]^q = 1.2 \times 10^{-2} \quad (\text{ii})$$

Dividing Eq. (ii) by Eq. (i)

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{k[0.4]^p [0.05]^q}{k[0.2]^p [0.05]^q} = \frac{1.2 \times 10^{-2}}{6.0 \times 10^{-3}}$$

$$\text{or } (2)^p = 2 \quad \text{or } p = 1.$$

Thus, the order with respect to NO₂ is 1

Now comparing experiments (2) and (3), we get

$$(\text{rate})_2 = k[0.4]^p [0.05]^q = 1.2 \times 10^{-2} \quad (\text{iii})$$

$$(\text{rate})_3 = k[0.8]^p [0.10]^q = 4.8 \times 10^{-2} \quad (\text{iv})$$

Dividing Eq. (iv) by Eq. (iii) we get

$$\frac{(\text{rate})_3}{(\text{rate})_2} = \frac{k[0.8]^p[0.10]^q}{k[0.4]^p[0.05]^q} = \frac{4.8 \times 10^{-2}}{1.2 \times 10^{-2}}$$

$$= (2)^p (2)^q = 4$$

We have obtained $p = 1$ so that

$$(2)^1 (2)^q = 4$$

$$= (2)^{q+1} = 2^2$$

$$q + 1 = 2$$

or $q = 2 - 1 = 1$

Thus, order wrt F_2 is 1

(i) Order of the reaction = $1 + 1 = 2$

(ii) Rate law for the reaction is

$$\text{Rate} = k[\text{NO}_2] [\text{F}_2]$$

(iii) Rate of reaction when $[\text{NO}_2] = 0.5 \text{ mol L}^{-1}$ and $[\text{F}_2] = 0.60 \text{ mol L}^{-1}$

For this, let us first calculate the value of k from the first experiment.

$$\text{Rate} = k[\text{NO}_2] [\text{F}_2]$$

$$6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} = k (0.20 \text{ mol L}^{-1}) \times (0.05 \text{ mol L}^{-1}).$$

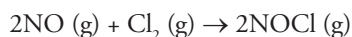
$$\text{or } k = \frac{6.0 \times 10^{-3}}{0.20 \times 0.05} \text{ mol L}^{-1} \text{ min}^{-1} = 0.6 \text{ mol L}^{-1} \text{ min}^{-1}$$

Substituting the value of k , $[\text{NO}_2]$ and $[\text{F}_2]$

$$\text{Rate} = 0.6 \times 0.5 \times 0.60 = 0.18 \text{ mol L}^{-1} \text{ min}^{-1}.$$

Practice problems

1. Three experiments were performed for the following reaction:



The following data were obtained

Experiment	Initial concentration		Initial rate $\text{mol L}^{-1} \text{s}^{-1}$
	$[\text{Cl}_2]$	$[\text{NO}]$	
I	0.02	0.01	2.40×10^{-4}
II	0.02	0.03	2.16×10^{-3}
III	0.04	0.03	4.32×10^{-3}

Determine

- (i) Order with respect to Cl_2 and NO
- (ii) Rate law
- (ii) Rate constant.

[Ans (i) 1, 2, (ii) $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$, (iii) $1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$]

2. The half-life periods, for the thermal decomposition of phosphine at three different pressures are given below

Initial pressure (mm)	707	79	37.5
Half-life (s)	84	84	83.

Calculate the order of the reaction.

[Ans first order]

3. The catalytic decomposition of nitrous oxide by gold at 900°C and an initial pressure of 200 mm was 50% complete in 53 min and 73% complete in 100 min. Find the order of the reaction.
4. For a reaction between NO and H_2 , the rates of decrease in the pressure of NO were 1.50 and 0.25 mm s^{-1} , when the pressure of gas were 359 and 152 mm, respectively (the pressure of H_2 was kept constant). Find the order of the reaction with respect to NO .

[Ans Order wrt $\text{NO} = 2$. Van't Hoff differential method is illustrated here. The rate wrt NO is directly proportional to $[\text{NO}]^n$, where $n = \text{order}$. Thus, $1.50 \propto (359)^n$ and $0.25 \propto (152)^n$ using pressure instead of concentration].

5. For a certain reaction at constant temperature, a concentration of $3.63 \times 10^{-2} \text{ mol L}^{-1}$ of the reactant was reduced to half the value in 440 s, when the initial concentration was $8.80 \times 10^{-2} \text{ mol L}^{-1}$, the half-life period was 205 s. Find the order of the reaction.

[Ans $1.8625 \approx 2$]

13.12 Concept of Activation Energy

You must have observed that generally chemical reactions do not occur unless some extra energy is supplied to the reacting molecules. Have you ever observed coal burning on its own or hydrogen and oxygen reacting to form water all by itself? The answer is No! Remember that all molecules possess some kinetic energy at room temperature. This energy is called the average kinetic energy of the molecules. This energy may not be sufficient to bring about the chemical reaction. The energy required for a chemical reaction to occur is equal to the threshold energy. Hence, some extra energy is to be provided to the reactant molecules to enable them to form products. This extra energy over and above the average kinetic energy of the molecules is called the activation energy E_a . This energy activates the molecules for product formation. Thus,

Activation Energy = Threshold Energy – Average kinetic energy of the reacting molecule.

Activation energy has an important role in deciding the rate of the reaction. If a reaction has low activation energy then a large number of molecules will be able to acquire it; therefore, the fraction of effective collisions will be high and hence the reaction will be fast. On the other hand, if a reaction has high activation energy then only few molecules will be able to acquire it, thereby reducing the fraction of effective collisions. Hence, the reaction will proceed slowly.

Thus

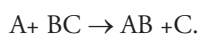
Low activation energy — fast reactions

High activation energy — slow reactions.

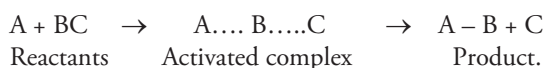
Activated complex state or transition state

When the molecules possessing energy equal to activation energy collide, the atomic configuration of the species formed at this stage is different from the configuration of either reactants or products. This stage is called the **transition state or activated state** and the specific configuration of this state is called the **activated complex**.

For example, consider the following reaction:



If the reaction occurs in a single step, then as A collides with B an intermediate stage arises in which the bond between A and B is partially formed and at the same time the old bond between B and C is partly broken. In this intermediate stage, all the three atoms A, B and C are weakly linked together. This state is the activated state and the intermediate compound is termed as the activated complex.



The activated complex is unstable and has a higher potential energy than the reactants or the products. Thus, before the reactants convert into products they have to cross a potential energy barrier.

This can be depicted graphically as shown in Figure 13.7.

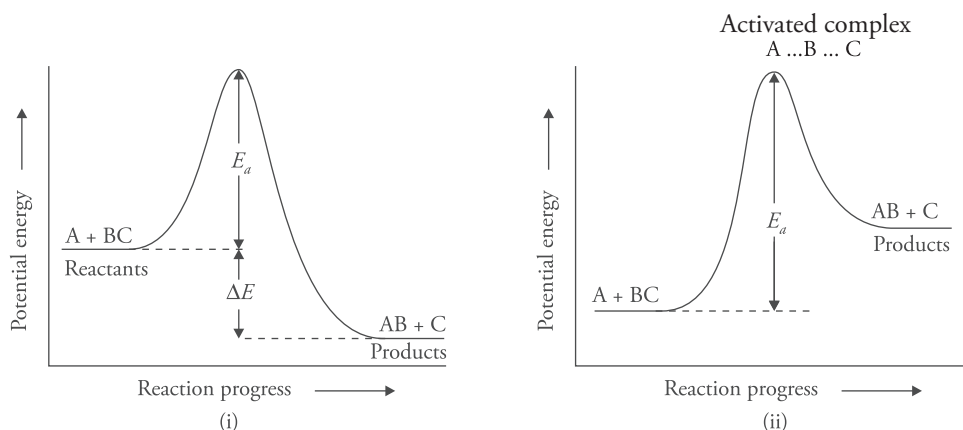


Figure 13.7 Potential energy profile for (i) exothermic reaction and (ii) endothermic reaction

The height of the barrier represents the activation energy E_a of the reaction and the configuration of the atoms at the maximum in the potential energy profile is called transition state. The energy needed to climb this hill comes from the kinetic energy of colliding molecules. If the collision

energy is less than E_a , the reactant molecules are unable to cross this barrier and they simply collide and bounce back. On the other hand, if the collision energy is equal to the activation energy E_a then the reactant molecules are able to cross this potential energy barrier and product formation takes place.

13.13 Variation of Reaction Rates with Temperature – Arrhenius Equation

The rate of a chemical reaction increases with the rise in temperature and it has been found that it becomes almost double for every 10 °C rise in temperature. This is known as the temperature coefficient, which may be defined as the ratio of rate constants of the reaction at two temperatures differing by 10 °C. Thus,

$$\text{Temperature coefficient} = \frac{\text{Rate constant } (T + 10^\circ \text{C})}{\text{Rate constant at } T^\circ \text{C}}$$

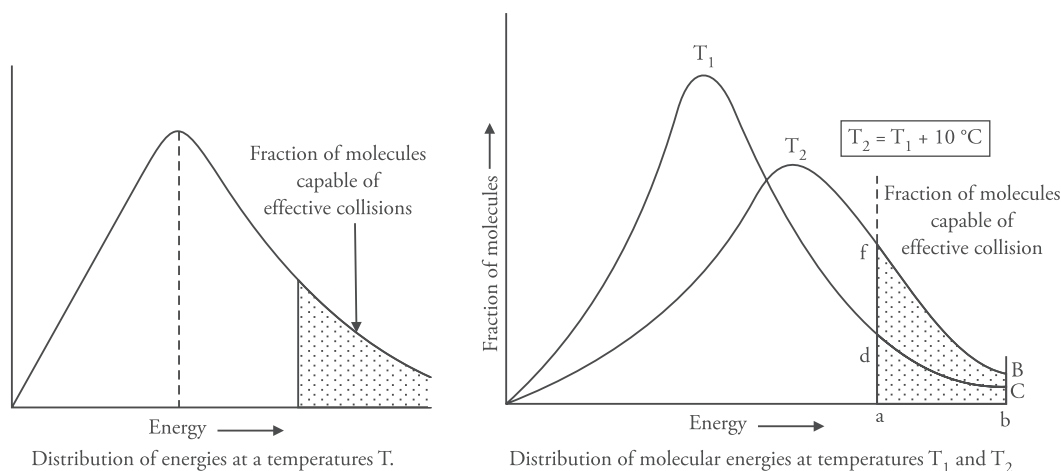


Figure 13.8 Variation of reaction rate with temperature

The curve shows that at higher temperature the curve is shifted towards the right indicating that at higher temperatures the molecules have higher energies. Since the rate of reaction depends on effective collisions, that is, collisions with sufficient energy and proper orientation (to be discussed in collision theory of reaction rates); hence, as seen from the graph the number of effective collision doubles on increasing the temperature by 10 °C; therefore, the rate of reaction also doubles.

Arrhenius equation and calculation of activation energy Swedish chemist Arrhenius in 1889 gave a method for expressing the influence of temperature on reaction velocity. He proposed a quantitative relationship between rate constant and temperature:

$$k = Ae^{-E_a/RT} \quad (1)$$

where k is the rate constant, A is the pre-exponential factor which is related to the frequency of collision, E_a is the activation energy or the energy barrier which the reactants must cross to form products, R is the gas constant and T is the temperature in K.

Taking logarithm of both sides,

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

Converting to the base 10 ($\ln x = 2.303 \log_{10} x$), we get

$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

$$\log k = \log A - \frac{E_a}{2.303RT} \quad (3)$$

The above equation shows that the value of k decreases as activation energy increases; hence, the rate of reaction decreases with the rise in activation energy.

Calculation of activation energy

The Arrhenius equation is in the form of $y = mx + c$, which represents a straight line.

$$\log k = \log A + \left(\frac{-E_a}{2.303R} \right) \left(\frac{1}{T} \right)$$

↓
y

↓
c

↓
m

↓
x

A plot of $\log k$ against $1/T$ is a straight line as shown in Figure 13.9. The intercept is equal to $\log A$ and the slope is equal to $-E_a/2.303 R$.

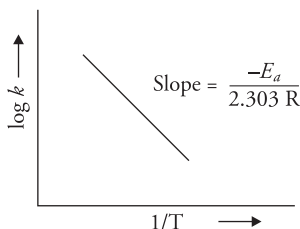


Figure 13.9 Plot of $\log k$ vs $1/T$ to calculate activation energy

$$\text{Slope} = -E_a/2.303 R.$$

Thus, knowing the slope and gas constant R , activation energy can be calculated as

$$E_a = -2.303 R \times \text{Slope}.$$

Alternative method E_a can be determined by measuring the value of rate constant at two different temperatures. If the rate constants at temperatures T_1 and T_2 are k_1 and k_2 , respectively, then at temperature T_1

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \quad (1)$$

And at temperature T_2

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2} \quad (2)$$

Subtracting Eq. (2) from Eq. (1), we get:

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3)$$

Solved Examples

1. The velocity constant for the decomposition of nitrous oxide is 5.16×10^4 at 1125 K and 3.76×10^3 at 1085 K. Calculate the activation energy for the reaction.

Solution

According to Arrhenius equation:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\therefore \log \frac{5.16 \times 10^4}{3.76 \times 10^3} = \frac{E_a}{2.303 \times 1.987} \left(\frac{1125 - 1085}{1125 \times 1085} \right)$$

$$\log \frac{51.6}{3.76} = \frac{E_a}{2.303 \times 1.987} \left(\frac{40}{1220625} \right)$$

$$1.13746 = \frac{E_a}{4.5761} \times 3.277 \times 10^{-5}$$

$$E_a = \frac{1.13746 \times 4.5761}{3.277 \times 10^{-5}} = 1.588 \times 10^5 \text{ cal mol}^{-1}$$

2. At 300 K, a first-order reaction is 50% completed in 20 min. At 350 K the same reaction takes 5 min for 50% completion. Calculate the energy of activation of the reaction.

Solution

$$k_1 (\text{at } 300\text{K}) = \frac{0.693}{t_{1/2}} = \frac{0.693}{20 \text{ min}}$$

$$k_2(\text{at } 350\text{K}) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5\text{ min}}$$

$$\frac{k_2}{k_1} = \frac{0.693}{5} \times \frac{20}{0.693} = 4$$

$$\text{now, } \log \frac{k_2}{k_1} = \log 4 = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{350 - 300}{350 \times 300} \right)$$

$$0.6020 = \frac{E_a}{2.303 \times 8.314} \left(\frac{50}{350 \times 300} \right)$$

$$E_a = \frac{0.6020 \times 2.3030 \times 8.314 \times 350 \times 300}{50} = 24206 \text{ J mol}^{-1}$$

3. The reaction

$2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ has an activation energy of 110 kJ mol^{-1} . At 400°C , the rate constant is $7.8 \text{ mol}^{-1} \text{ L s}^{-1}$. Find the value of rate constant at 430°C .

Solution

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$E_a = 110 \text{ kJ mol}^{-1} = 110 \times 10^3 \text{ J mol}^{-1} \quad R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$k_1 = 7.8 \text{ mol}^{-1} \text{ L s}^{-1} \quad T_1 = 400 + 273 = 673 \text{ K}$$

$$k_2 = ? \quad T_2 = 430 + 273 = 703 \text{ K}$$

Substituting the values

$$\log \frac{k_2}{7.8} = \frac{110 \times 10^3}{2.303 \times 8.314} \left(\frac{703 - 673}{703 \times 673} \right)$$

$$\log \frac{k_2}{7.8} = 0.3643, \quad \text{or} \quad \frac{k_2}{7.8} = \text{Anti log}(0.3643)$$

$$\frac{k_2}{7.8} = 2.31 \quad \text{or} \quad k_2 = 2.31 \times 7.8 = 18.04 \text{ mol}^{-1} \text{ L s}^{-1}$$

4. The values of A and E for a certain reaction are $4.0 \times 10^{13} \text{ s}^{-1}$ and 98.6 kJ mol^{-1} , respectively. If the reaction is of first order, then using the Arrhenius equation calculate the temperature at which its half-life period will be 10 min.

Solution

$$A = 4.0 \times 10^{13} \text{ s}^{-1} \quad E_a = 98600 \text{ J mol}^{-1} \quad t_{1/2} = 10 \text{ min} = 600 \text{ s} \quad T = ?$$

According to Arrhenius equation: $k = Ae^{-\frac{E_a}{RT}}$

Taking log on both sides,

$$\log k = \log A - \frac{E_a}{2.303RT} \quad \text{or} \quad \log \frac{k}{A} = -\frac{E_a}{2.303RT}$$

Calculation of k

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{600} = 1.155 \times 10^{-3} \text{ s}^{-1}$$

$$\log \frac{1.155 \times 10^{-3}}{4.0 \times 10^{13}} = -\frac{98600}{2.303 \times 8.314 T} \quad (\because R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$-16.5395 = -\frac{98600}{2.303 \times 8.314 T}$$

$$\text{or} \quad T = 311.35 \text{ K.}$$

5. The rate constant for the first-order reaction is given by

$$\log k(\text{in s}^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

What is the value of (i) activation energy and (ii) k at 670 K=?

Solution

$$\log k = \log A - \frac{E_a}{2.303RT} = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

Comparing we have

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4}{T}$$

$$E_a = (1.25 \times 10^4 \text{ K})(2.303)(8.31 \text{ J mol}^{-1} \text{ K}^{-1}) = 239 \times 10^3 \text{ J mol}^{-1} = 239 \text{ kJ mol}^{-1}$$

(ii) Now,

$$\log k = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{670 \text{ K}}$$

$$\log k = -4.32$$

$$k = \text{Antilog}(-4.32) = 4.8 \times 10^{-5} \text{ s}^{-1}.$$

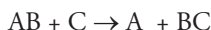
Practice problems

- Find the activation energy of the reaction if the first-order rate constant becomes eight times on increasing the temperature from 300 to 450 K.
[Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] [Ans 15.5 kJ mol^{-1}]
- The half-life of a first-order reaction is 30 min at 27°C and 10 min at 47°C . Determine the activation energy of the reaction. [Ans $E_a = 43.8 \text{ kJ mol}^{-1}$]
- The first-order decomposition of N_2O_4 into NO_2 has a k value of $4.5 \times 10^3 \text{ s}^{-1}$ at 1°C and an energy of activation of 58 kJ mol^{-1} . At what temperature its half-life would be $6.93 \times 10^{-5} \text{ s}$. [Ans 282.873 K]

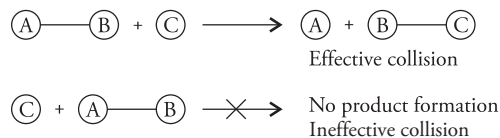
13.14 Theories of Reaction Rates

- Collision theory** According to this theory, a reaction will occur only if the reacting molecules collide with each other. The number of collisions can be expressed in terms of collision frequency, which can be defined as *the number of collisions per second per unit volume of the reaction mixture. It is expressed by the symbol z .* Under normal conditions of temperature and pressure, the collision frequency of binary collision is very high (of the order of 10^{25} to 10^{28}). If all collisions were to lead to product formation, the rate of the reaction would be very high and the reaction would be completed very fast. However, actually it is not so. Most chemical reactions proceed moderately or slowly. This means that all the collisions do not lead to product formation. *The collisions that actually lead to product formation are called 'effective collisions'.* In order for a molecular collision to be effective, it must meet two conditions: (i) energy barrier and (ii) orientation barrier.
 - Energy barrier** For the formation of products the bonds between the reactant molecules are to be broken. The breaking of bonds requires energy. Hence, the colliding molecules must have a minimum amount of energy that should be greater than the energy required to break the bonds between the reactant molecules. This minimum energy that the colliding molecules must possess is known as the **threshold energy**. Only those collisions will lead to product formation, which possess energies greater than the threshold energy.
 - Orientation barrier** It is not essential that all the collisions between the reactant molecules with sufficient energy would lead to product formation. For an effective collision, it is necessary that apart from having sufficient energy the molecules should be properly oriented.

Consider the reaction,



This reaction will occur only if C approaches AB from the B end. If it approaches the reactant from the A end of the molecule then product formation will not occur and the molecule will simply bounce back.

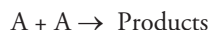


Thus, the fraction of effective collisions determines the rate of the reaction. Effective collisions are collisions with sufficient energy and proper orientation.

\therefore Rate of reaction = Collision frequency \times fraction of effective collisions.

Mathematical formulation of collision theory

The collision theory is based on the kinetic theory of gases and applies mainly to bimolecular reactions in the gaseous phase. It assumes that the colliding molecules are perfectly spherical hard spheres and the collision between them are perfectly elastic. To derive the rate law let us consider a simple bimolecular reaction



The reaction rate between two identical molecules is given by

$$\frac{dx}{dt} = z_{AA} e^{-E/RT} \quad \dots(1) \tag{1}$$

where z_{AA} is the collision frequency, that is, number of binary collisions per unit volume per second between two identical molecules in 1 mL of the gas and E is the activation energy of the process. According to the kinetic theory of gases, the reaction velocity is related to concentration by the relation

$$\frac{dx}{dt} \propto n_A^2 \quad \text{or} \quad \frac{dx}{dt} = kn_A^2 \tag{2}$$

where k is the specific rate constant and ' n ' is the concentration of the reactant. Comparing Eq. (1) with Eq. (2), we have:

$$k = \frac{z_{AA}}{n_A^2} e^{-E/RT} \quad \dots(3) \tag{3}$$

The collision frequency between the two similar molecules is given by simple kinetic theory of gas:

$$z_{AA} = \frac{1}{2} \left(\pi \sigma_{AA}^2 \right) \left(\frac{16kT}{\pi m_A} \right)^{1/2} n_A^2$$

where

σ_{AA} = collision cross-section

K = Boltzmann constant

T = Temperature

n_A = number of A molecules per unit volume

m_A = mass of A.

If the activation energy of the molecules is known, then Eq. (3) predicts the rate constant fairly accurately for simple molecules but deviations are found for complex molecules. For these reactions, the experimental values for rate constant are smaller than those predicted by Eq. (3). This is because simple kinetic theory considers every sufficiently energetic collision as an effective collision. However, if the energetic molecules do not approach with proper orientation, then product formation will not occur. To correct the above discrepancy, Eq. (3) was modified as:

$$k = P \frac{z_{AA}}{n_A^2} e^{-E/RT} \quad (4)$$

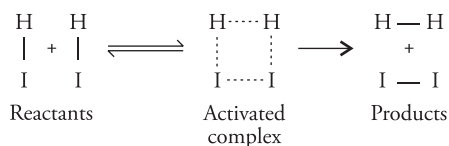
where P = probability factor or steric factor, which takes into account the fact that for an effective collision the molecules with sufficient energy should have proper orientation.

Limitation of collision theory

The major drawback of the collision theory is that it assumes the reacting species to be hard spheres and ignores the internal structure of the molecules. Hence, it fails to explain satisfactorily probability factor at the molecular level. Moreover, the collision diameters calculated are too imprecise and overestimated. The collision theory says nothing about the cleavage and formation of bonds involved in the reaction.

2. **Transition state theory or Absolute Reaction Rate Theory** This theory proposed by Pelzer and Minger in 1932 and later extensively developed by Eyring and his collaborators (1935) provides a greater insight into the details of a reaction on a molecular scale. It also enables us to calculate the rate constant with considerable accuracy. The important postulates of this theory are as follows:

- (i) The reactant molecules before forming products pass through an intermediate state called the transition state or the activated complex. In this complex, the reactant and the product molecules are weakly linked.



- (ii) The activated complex is an unstable state with potential energy greater than that of the reactants and products. The potential energy of the activated complex is maximum.

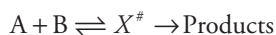
- (iii) Fundamental assumption of transition state theory (and one that differentiates it from collision theory) is that the reactants are always in equilibrium with the activated complex.



- (iv) Activated complex is like a normal molecule in every respect, but, apart from having three translational degrees of freedom, it has an additional fourth degree of freedom along the reaction coordinate. The activated complex decomposes along the fourth degree of freedom to form the products.



The above postulates can be put as



A and B are reactants and $X^{\#}$ represent the activated complex.

- (v) The energy changes in the conversion of reactants to products via the activated complex are represented in Figure 13.10.

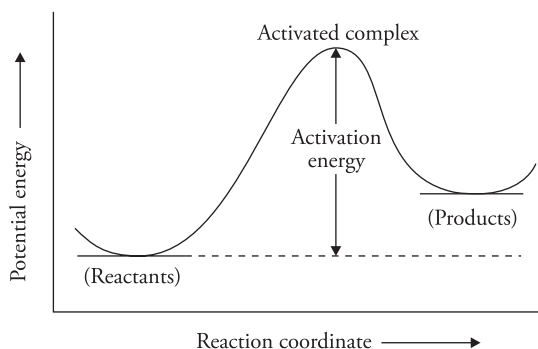


Figure 13.10 Activation energy required for the formation of the activated complex

The rate of reaction is equal to the concentration of the activated complex at the top of the energy barrier multiplied by the frequency ν of crossing the barrier.

Rate of reaction = number of activated complexes decomposing to form the product

$$\text{Rate of reaction} = \nu [X^{\#}] \quad (5)$$

The value of $[X^{\#}]$ can be obtained by considering the equilibrium between the reactants and the activated complex.

$$k^{\#} = \frac{[X^{\#}]}{[A][B]} \quad \text{or} \quad [X^{\#}] = k^{\#} [A][B]$$

$k^{\#}$ = equilibrium constant

$[A]$ and $[B]$ = concentration of the reactants

Placing the values of $[X^{\#}]$ in Eq. (5), we have

$$\text{Rate} = v k^\# [A][B]$$

$$= k [A][B]$$

where $k = v k^\#$

Thus, the rate can be calculated if the value of v and $k^\#$ are known.

Thermodynamic Formulation of Transition State Theory:

Eyring showed that the rate constant (k) for any reaction (irrespective of its molecularity) is given by

$$k = \frac{k_B T}{h} K^\# \quad (1)$$

where k_B is the Boltzmann constant, h is the Planck's constant, T is the absolute temperature and $K^\#$ is the equilibrium constant for the formation of activated complex. If R is used instead of k_B then the equation becomes $k = \frac{RT}{N_A h} K^\#$ where N_A is the Avogadro's number.

As studied earlier, the equilibrium constant for the reaction



The equilibrium constant $K^\#$ can be expressed in terms of $(\Delta G^\#)$, termed as the Gibbs free energy of activation. Hence we can write

$$(\Delta G^\#) = -RT \ln K^\#$$

$$\text{or } K^\# = e^{-\Delta G^\# / RT} \quad (2)$$

Since, $\Delta G^\# = \Delta H^\# - T\Delta S^\#$ we get

$$K^\# = e^{-(\Delta H^\# - T\Delta S^\#) / RT} \quad (3)$$

where $\Delta H^\#$ and $\Delta S^\#$ are the changes in enthalpy and entropy for the activated complex.

Substituting the value of $K^\#$ from Eq. (3) in Eq. (1), we get

$$k = \frac{k_B T}{h} e^{-(\Delta H^\# - T\Delta S^\#) / RT}$$

$$\text{or } k = \frac{k_B T}{h} e^{\Delta S^\# / R} e^{-\Delta H^\# / RT} \quad (4)$$

Equation (4) is known as the Eyring equation.

Comparing (Eq. 4) of transition state theory with Arrhenius theory, we observe that

$$A = \frac{k_B T}{h} \cdot e^{\Delta S^\ddagger / R} \text{ and } E_a = \Delta H^\ddagger \quad (\text{i.e., enthalpy of activation is equal to the energy of activation})$$

On comparing with collision theory

$$k = pZ e^{-\Delta E_a / RT}$$

$$\text{we find that } pZ = \frac{k_B T}{h} e^{\Delta S^\ddagger / R}$$

Thus probability factor is related to entropy of activation S^\ddagger .

13.15 Potential Energy of Surfaces

The collision theory and transition state theory explain chemical reactions on microscopic level by considering the energies and orientations of the reactants and products. These theories do not, however, consider the detailed interactions between the reactant molecules and product molecules as they approach each other and move away from each other. The potential energy surfaces explain chemical reactions by exploring these interactions.

Potential energy surfaces map the potential energy of a molecule as a function of its molecular geometry and position of atoms when they approach and move away from each other during bond formation and bond cleavage.

Consider an atom, its position in space is defined by three coordinates x , y and z . Similarly a molecule with N atoms has $3N$ nuclear coordinates to describe its position. For a non-linear molecule potential energy is a function of $3N - 6$ variables and for a linear molecule it is a function of $3N - 5$ variables. Let us discuss some examples. In a simple bimolecular collision between atoms A and B where $N = 2$, the transition state will be linear and hence potential energy is a variable of one function ($3N - 5 = 3 \times 2 - 5 = 1$), the interatomic distance R . The potential energy curve is obtained as shown in Figure 13.11.

The curve obtained in Figure 13.11 is a simple Morse curve. As the two atoms approach each other the potential energy decreases till it reaches a minima (the equilibrium bond length). On trying to bring the atoms further close to each other the repulsive forces increase and the energy goes up.

Now let us consider the interaction between a molecule AB and an atom C. In this case ($N = 3$) potential energy is a function of $3 \times 3 - 6 = 3$ variables. These variables are the two interatomic distances R_{ab} and R_{bc} and angle θ (angle A – B – C). Since the potential energy in the above case is a function of these three variables, the plot of energy would be three dimensional surface requiring four dimensions to plot the surface. This will make the plot extremely complicated and difficult to visualise. Hence to simplify it we fix the bond angle by choosing a collinear molecule ($\theta = 180^\circ$). Now potential energy V is a function of two distances R_{ab} and R_{bc} only and this plot can be viewed as a three-dimensional plot.

The most investigated example of the above type is the reaction of $H + H_2 \rightarrow H_2 + H$. The reaction can be studied experimentally using isotopes $D + H_2 \rightarrow DH + H$ or ortho and para H_2

($H + \text{para } H_2 \rightarrow \text{ortho } H_2 + H$). However, we, in our further discussion shall express the reaction as $H_a + H_b H_c \rightarrow H_a H_b + H_c$.

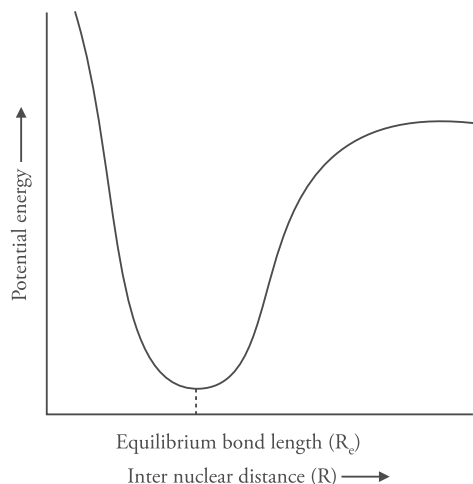


Figure 13.11 Morse curve

The collision between H_a and H_bH_c is collinear $\theta = 180^\circ$. The potential energy surface for the above reaction is three dimensional, which is difficult to plot; hence, contour diagrams (equipotential energy curves) have become popular. Contour plot of $H_a + H_bH_c \rightarrow H_aH_b + H_c$ is shown in Figure 13.12.

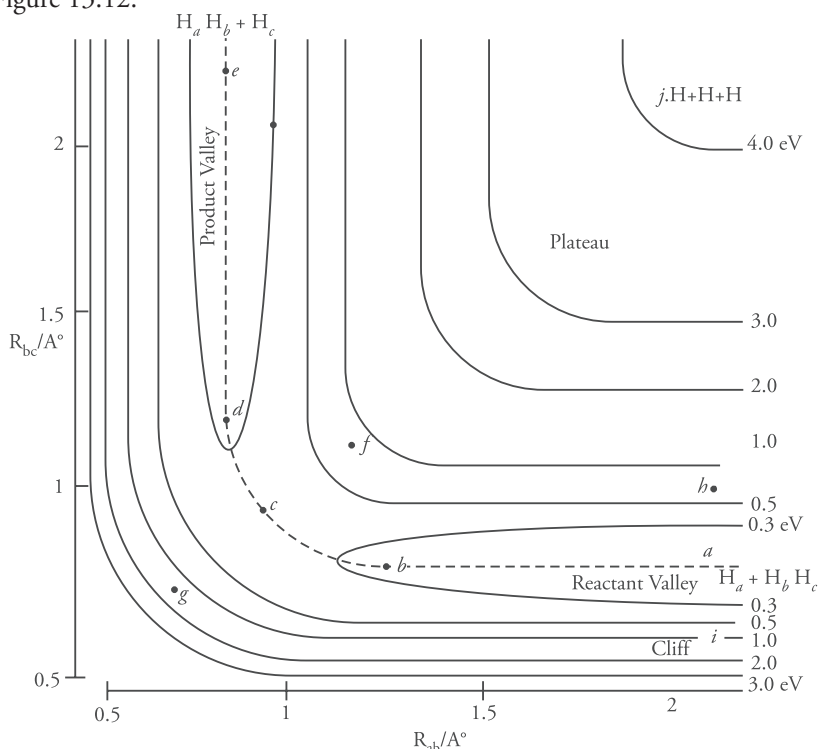


Figure 13.12 Contour plot for $H + H_2$ potential energy surface for $\theta = 180^\circ$ [Data from R. N Porter and M. Karplus. *J. Chem Phys.* 40, 1105 (1964)]

The valley to the right of the contour map is the reactant valley where the point a corresponds to reactants $H_a + H_bH_c$. The potential energy at a has been taken as zero and it depicts the equilibrium bond length in H_bH_c (0.74 \AA). R_{ab} at this point is large indicating that the atom H_a is far from the molecule H_bH_c . Similarly the valley perpendicular to the reactant is the product valley. The point e in the product valley corresponds to products $H_aH_b + H_c$. Here the value of R_{bc} is large indicating that H_c is far from the molecule H_aH_b . The energy at point e is also taken as zero.

The region around point j is the plateau where H_a , H_b and H_c are all widely separated as both R_{ab} and R_{bc} are large. This region does not play any part in the reaction. Since the atoms are very far from each other in this region hence changing R_{ab} or R_{bc} hardly affects the potential energy V .

Consider the points h , a , i on the graph. Along these points, R_{ab} is constant but R_{bc} varies. The potential energy increases from a to h and a to i , hence a lies at the bottom of the reactant valley and represents the equilibrium bond distance in H_bH_c . Moreover, along the line $h a i$ we get a ground state diatomic potential energy curve (similar to the Morse curve in Fig. 13.12) for H_2 . Similarly point e lies at the bottom of the product valley perpendicular to the reactant valley.

The dotted line $abcde$ joins the path of minimum potential energy between reactants and products. At point b , H_aH_b bond is slightly formed and H_bH_c bond lengthens slightly (becomes slightly weak). At point c , $R_{ab} = R_{bc}$ hence $H_a - H_b$ bond is half formed and $H_b - H_c$ bond is half broken. At d , $H_b - H_c$ distance increases further and H_a comes closer to H_b , whereas at e the reaction is completed where $H_a - H_b$ bond is formed and H_c moves away. The potential energy decreases from $a \rightarrow b \rightarrow c$ and further increases. Thus c is the maximum point on the minimum energy curve and is termed as the *saddle point* as the surface of c resembles a saddle. The order of potential energy is as follows: $V_c < V_f$ and $V_c < V_g$ but $V_c > V_b$ and $V_c > V_d$. As one moves from a to c there is a high energy cliff on the left and a high energy plateau on the right. The dotted path passing through the saddle point provides low energy path to move from the reactant valley to the product valley.

Although we have considered a collinear collision but similar contour plots can be drawn for other values of θ . The configuration of the colliding articles at the saddle point is called the transition state. The transition state for $H + H_2$ is linear and symmetric with each bond distance equal to 0.93 \AA (bond distance in H_2 molecule is 0.74 \AA). The potential energy difference between the transition state and reactants (omitting zero point vibrational energy) is called the activation energy which is 10 kcal/mol for $H_a + H_bH_c \rightarrow H_aH_b + H_c$. This energy is much less than the energy required to break the H_2 bond (110 kcal/mol) because in the transition state as $H_b - H_c$ bond is breaking $H_a - H_b$ bond is being formed and energy released during bond formation compensates for the energy required to break the bond. It is important here to note that the transition state occurs at the maximum point on the minimum energy path between the reactants and products.

Potential Energy Surface of H_2F

Figure 13.13 gives the potential energy contours for a collinear collision ($\theta = 180^\circ$) for the reaction $F + H_2 \rightarrow H + HF$. The figure is less symmetrical compared to that of H_3 because unlike H_3 , here the reactants and products are different from each other.

The geometry of the saddle point (transition state) was earlier thought to be linear with $R(\text{HF}) = 1.54 \text{ \AA}$ and $R(\text{HH}) = 0.77 \text{ \AA}$ compared with $R(\text{HH}) = 0.74 \text{ \AA}$ in isolated H_2 molecule and $R(\text{HF}) = 0.93 \text{ \AA}$ in HF. However, it was later found that transition state is bent at about 65° and the barrier is $\frac{1}{2}$ kcal/mol less than for linear transition state. The barrier height for the reaction $\text{F} + \text{H}_2 \rightarrow \text{H} + \text{HF}$ is 1.7 kcal/mol.

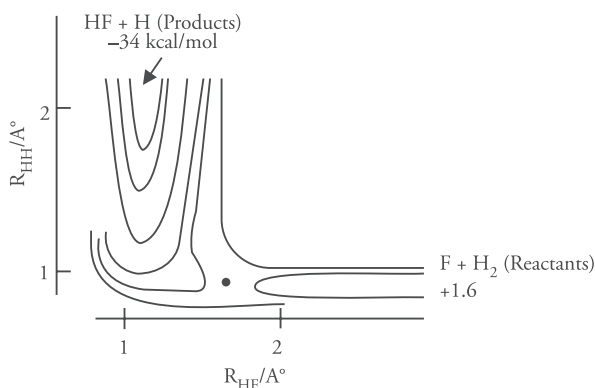


Figure 13.13 Contour diagram for $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$ for $\theta = 180^\circ$. [Adapted from C. F. Bender, S. V. O'Neil, P. K. Pearson and H. F. Schaefer, *Science*, 176, 1412-1414 (1972). Original figure copyright 1972 by American Association of Advancement of Science]

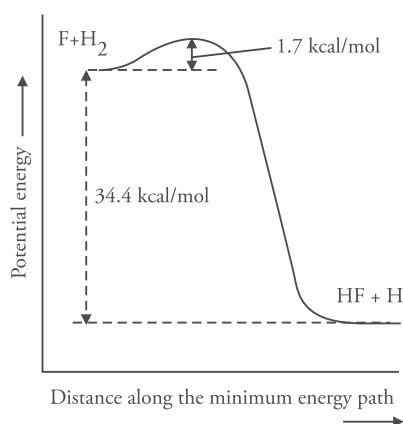


Figure 13.14 Potential energy versus distance d along the minimum energy path for the reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$

Potential Energy Surface of $\text{HC} + \text{N}$

Since the HCN molecule is very stable hence the $\text{HC} + \text{N}$ potential energy surface is markedly different from the $\text{H} + \text{H}_2$ potential energy surface. Unlike the latter potential energy surface, the

HC + N potential energy surface does not have a saddle point (which is usually 0.2 to 2 eV higher than the saddle point), on the other hand it has a deep hole at about 10 eV at a distance $R_{\text{CH}} = 1 \text{ \AA}$ and $R_{\text{CN}} = 1 \text{ \AA}$. This is because of the stability of HCN molecule. Since the $\text{C} \equiv \text{N}$ is stronger than $\text{C} - \text{H}$ bond, the CN end lies lower than the CH end, and HCN being more stable than both these ends forms a well.

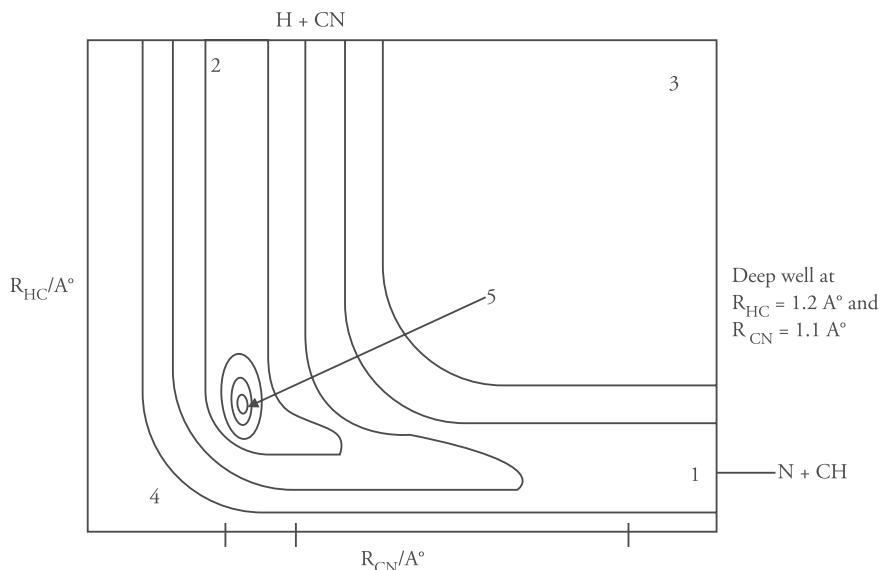


Figure 13.15 Potential energy surface of H + CN

Trajectories on a Potential Energy Surface

A trajectory defines the path followed by the atoms and molecules on moving from the reactant valley to the product valley along the minimum energy path of the potential energy surface. The starting point of a reaction is in the reactant valley where one of the reactants is at a minimum potential energy and the other reactants are far away. For a reaction between an atom H_a and molecule H_bH_c ; as H_a approaches H_bH_c with H_bH_c distance nearly constant we move towards the transition state in the valley with each point corresponding to the collinear configuration of $H_a \dots H_bH_c$. The path of the reactants as a function of time is followed on the computer by integrating the forces obtained from the potential energy surface. A trajectory that leads to product formation crosses the energy barrier to the product valley and is termed as the reactive trajectory. Rate constant for a reaction at a particular temperature is obtained by calculating the trajectories and averaging using the Boltzmann constant. Although the motion of atoms obeys quantum mechanics but it is extremely difficult to solve the Schrodinger wave equation to compute the trajectories hence the classical approach is followed. The results obtained by classical trajectories are fairly accurate except when very light atoms are involved.

The classical trajectories for the linear collision ($\theta = 180^\circ$) $H_a + H_bH_c \rightarrow H_aH_b + H_c$ is shown in Figure 13.16.

In Figure 13.16 a, the vibrational energy level of the molecule H_bH_c is zero hence the trajectory of transition state oscillates about the minimum energy path (shown by dashed line in the figure) and the molecule does not cross the barrier precisely at the saddle point. Another reason why the minimum energy path is not precisely followed is that all the collisions are not strictly collinear ($\theta \neq 180^\circ$). The vibrations of product valley are wide indicating that H_aH_b has been produced in excited vibrational level. Figure 13.16 b shows a non-reactive trajectory.

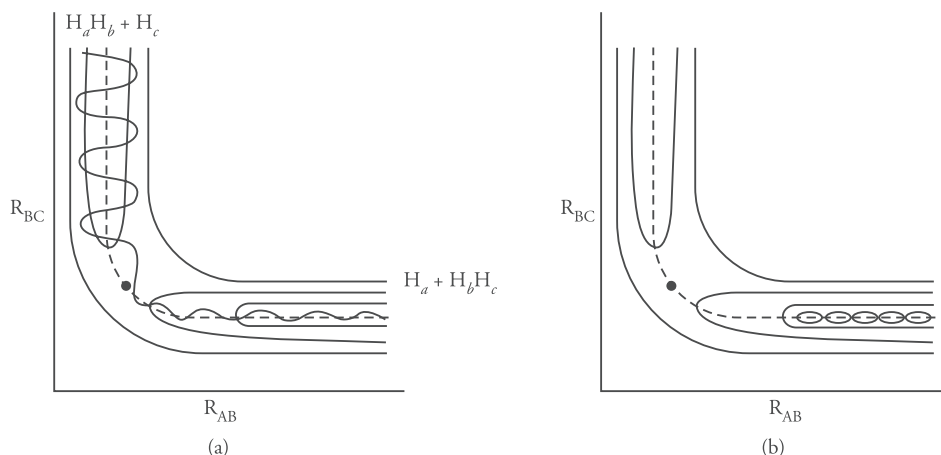


Figure 13.16 Classical trajectories for the reaction $H_a + H_bH_c \rightarrow H_aH_b + H_c$. Dot in the figure represents the saddle point. (a) A reactive collision, (b) A non-reactive collision

A good way to show the formation of products is to plot interatomic distances as a function of time. In Figure 13.16a, the atom H_a approaches the molecule H_bH_c (distance R_{ab} and R_{ac} decreases) and then it moves away without reacting (distance R_{ab} and R_{ac} increases). This shows that no reaction has occurred. There is continuous fluctuation of H_bH_c due to zero point vibration. Figure 13.17 shows that H_a approaches H_bH_c and collides at 30 fs (femtoseconds). After this R_{bc} goes to infinity showing that $H_b - H_c$ bond has broken and R_{ab} fluctuates about equilibrium; H_2 bond distance being 0.74 \AA indicating that H_a is bonded to H_b . We note that at 40 fs atom H_c is closer to H_b in H_aH_b , but at 50 fs it is closer to H_a . This indicates that the product molecule is rotating. Since most collisions are non collinear, hence the trajectory calculations for $H + H_2$ require the knowledge of R_{ab} , R_{bc} and θ to calculate rate constant. In $H + H_2$ trajectories the energy to overcome the potential energy barrier comes from the vibrational energy of the reactants; rotational energy does not contribute. For $H + H_2$ collision most of the collisions are non linear at an approximate approach angle of 160° . The rate constants calculated from classical trajectories are in fair agreement with the experimental values; however, the errors generally arise due to inaccuracies in the potential energy surfaces. Figure 13.18 shows the non-reactive trajectory for generally $H + H_2$ reaction.

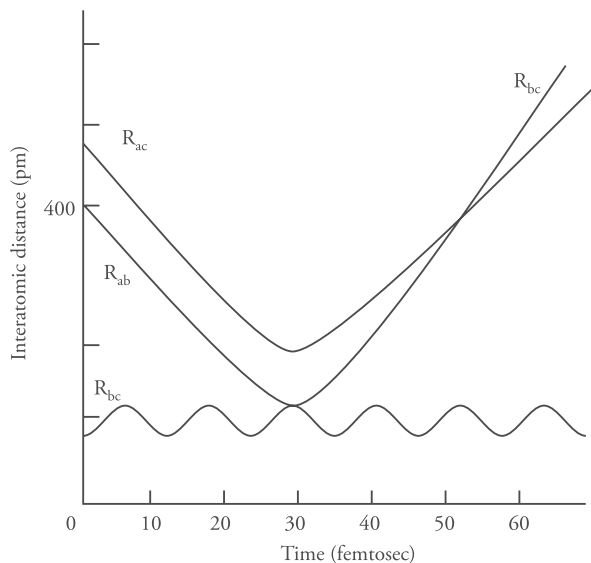


Figure 13.17 *Reactive trajectory of $H + H_2$ reaction*

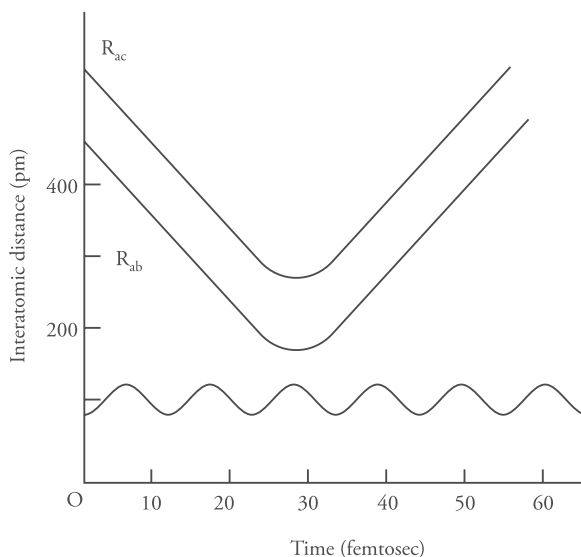


Figure 13.18 *Non-reactive trajectory of $H + H_2$ reaction*

13.16 Catalysis

The term catalysis was introduced by J.J. Berzelius (1835). It describes the influence of a foreign substance on the rate of a reaction. This foreign substance referred to as the catalyst alters (increases or decreases) the reaction rate without itself being used up in the reaction.

The term *catalyst* is generally used to express acceleration. According to Ostwald (1985), a catalyst is defined as a substance that changes the rate of the reaction without affecting the overall energetics of the reaction.

Characteristics of catalysts

The characteristics of catalysts are as follows.

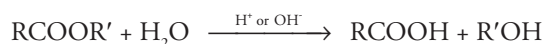
1. **Mass and composition of a catalyst remains unchanged at the end of the reaction** The quantity of a catalyst remains unchanged after the reaction. However, it may undergo physical change.

For example, manganese dioxide that is used to catalyse decomposition of potassium chlorate is in the form of large crystals in the beginning but changes into fine powder in the end. Similarly, platinum gauze used in the oxidation of ammonia becomes quite rough after some weeks.

As catalyst undergoes physical change, it implies that it participates in the chemical reaction but is regenerated in the end.

2. **Required in small amounts** Only a small amount of catalyst is sufficient to bring appreciable change in the reaction. For example, 1 g of copper (II) ions in 10⁹ L is sufficient to catalyse the oxidation of sodium sulphite by oxygen. Similarly, decomposition of hydrogen peroxide is catalysed by a very low concentration of colloidal platinum (1 mole in 10⁸ L).

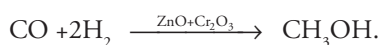
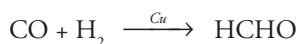
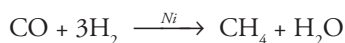
However, in homogeneous catalysis the rate of reaction is directly proportional to the concentration of the catalyst. For example, in acidic or alkaline hydrolysis of ester, the rate of reaction is proportional to the concentration of acid, which acts as a catalyst.



3. **Effect on equilibrium of a reversible reaction** A catalyst increases the rate of forward and backward reaction to the same extent and hence it helps in attaining equilibrium more quickly. However, the composition of the reaction mixture at equilibrium is not affected by the catalyst. The equilibrium constant remains unchanged.
4. **Inability to start a reaction** It is believed that catalyst only increases the rate of a reaction, it cannot start a reaction. However, this point is controversial. Ostwald (1895) said that catalyst cannot initiate a reaction but H.W. Armstrong (1885–1903) and T.W. Lowry (1925–1928) have suggested that certain reactions do not occur in the absence of a catalyst. For example perfectly dry H₂ and O₂ do not combine to form water, even if they are left in contact for years, but when little quantity of water is added as a catalyst the reaction proceeds quite rapidly. However, this point is still controversial.
5. **Specific in action** A catalyst is specific in action. A particular reaction is catalysed by a specific catalyst. The specific action of a catalyst can be compared to a lock and key. Just as a key opens a specific lock, each reaction is catalysed by a specific catalyst.

For example, MnO_2 catalyses decomposition of KClO_3 and not of KClO_4 .

6. **Nature of products is unaltered by the presence of catalyst** N_2 and H_2 always combine to form NH_3 irrespective of whether the catalyst is present or absent. Similarly, SO_2 and O_2 always combine to form SO_3 , whether the catalyst is present or not. However, there are certain exceptions also – for example, CO and H_2 form different products in the presence of different catalysts:



7. **Optimum temperature** The temperature at which the effect of catalyst is maximum is called the optimum temperature. For example, the optimum temperature for enzymes is 35–37 °C. At higher temperatures, they coagulate and lose their activity and at lower temperature also they are relatively inactive.
8. **Catalytic promoters** Substances that increase the activity of a catalyst are called catalytic promoters. For example, in the manufacture of NH_3 by Haber's process, finely divided iron acts as a catalyst, while molybdenum acts as a promoter.
9. **Catalytic poisons** Substances that inhibit or destroy the activity of a catalyst are called catalytic poisons or anticatalysts. For example, in the manufacturing of H_2SO_4 by contact process, a trace of As_2O_3 destroys the efficiency of spongy platinum.
10. **High surface area** Greater the surface area of a catalyst, greater will be its activity.

Type of catalysis

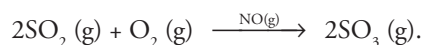
Generally there are two type of catalysis: (1) homogeneous catalysis and (2) heterogeneous catalysis.

1. **Homogeneous catalysis** In homogeneous catalysis, the catalyst, the reactants and the products are in the same phase. Homogeneous catalysis can occur in gaseous or liquid phase.
- (a) **In gaseous phase**

- (i) In atmosphere, the conversion of molecular oxygen to ozone is catalysed by nitric oxide in a gaseous phase (homogeneous catalysis).



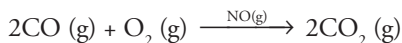
- (ii) In the manufacture of H_2SO_4 by lead chamber process, nitric oxide acts as the catalyst for the oxidation of SO_2 to SO_3



(iii) Decomposition of acetaldehyde is catalysed by iodine vapors.

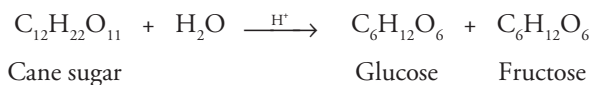


(iv) Nitric oxide catalyses the conversion of CO to CO₂ in the presence of O₂.



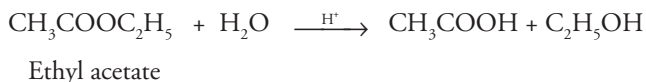
(b) **In liquid phase**

(i) The inversion of cane sugar is catalysed by a mineral acid



Here the catalyst, reactant and products are all in the liquid phase.

(ii) Hydrolysis of esters catalysed by acids:

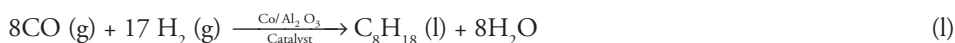


2. **Heterogeneous catalysis** In heterogeneous catalysis, the reactants and the catalyst exist in different phases. Generally, the catalyst is in solid phase and the reactants are either gases or liquids.

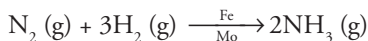
Examples of heterogeneous catalysis reactions

(a) **Catalysis involving gaseous reactants**

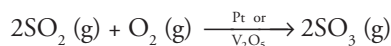
(i) In the synthesis of gasoline by Fischer–Tropsch process, the conversion of gaseous carbon monoxide and hydrogen to hydrocarbons such as octane (C₈H₁₈) is catalysed by solid catalysts like iron or cobalt coated on alumina (Al₂O₃).



(ii) In Haber's process for the manufacture of NH₃ gaseous nitrogen and hydrogen react in the presence of heated iron catalyst, which contains molybdenum as a promoter

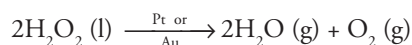


- (iii) In contact process for the manufacture of H_2SO_4 , gaseous sulphur dioxide is oxidised to sulphur trioxide in the presence of platinum or vanadium pentaoxide as catalyst



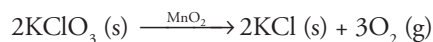
(b) **Heterogeneous catalysis involving liquid reactants**

The decomposition of hydrogen peroxide is catalysed by colloidal solution of gold and platinum.



(c) **Heterogeneous catalysis involving solid reactants**

Decomposition of potassium chlorate in the presence of solid MnO_2 , which acts as a catalyst.



Catalyst and activation energy

A question comes to our mind: How does a catalyst increase the rate of the reaction? To understand this, let us study the effect of catalyst on the activation energy of a reaction.

Catalyst and activation energy

As discussed earlier (Section 13.14), the collision theory says that those collisions lead to product formation in which the colliding molecules have a certain minimum energy called threshold energy. Collision between molecules with energy less than the threshold energy do not lead to product formation. Most molecules possess an average kinetic energy that is much less than the threshold energy. Extra energy is to be supplied to these molecules to enable them to reach up to the threshold energy level. This extra energy over and above the average kinetic energy of the molecules that the reactant molecules must acquire to change into products is called the activation energy E_a .

Thus,

Activation energy E_a = Threshold energy – Average kinetic energy of the molecules.

Effect of catalyst on activation energy

Catalyst provides an alternative route by entering into chemical combination with the reactants. This alternative route requires less energy of activation. We can compare the function of a catalyst to that of a tunnel in crossing a mountain. Crossing the mountain at its full height requires more energy. A tunnel in the mountain provides a low-energy pathway to cross the mountain.

Similarly, a catalyst also provides an alternative pathway to the reaction requiring lower activation energy (Fig. 13.19).

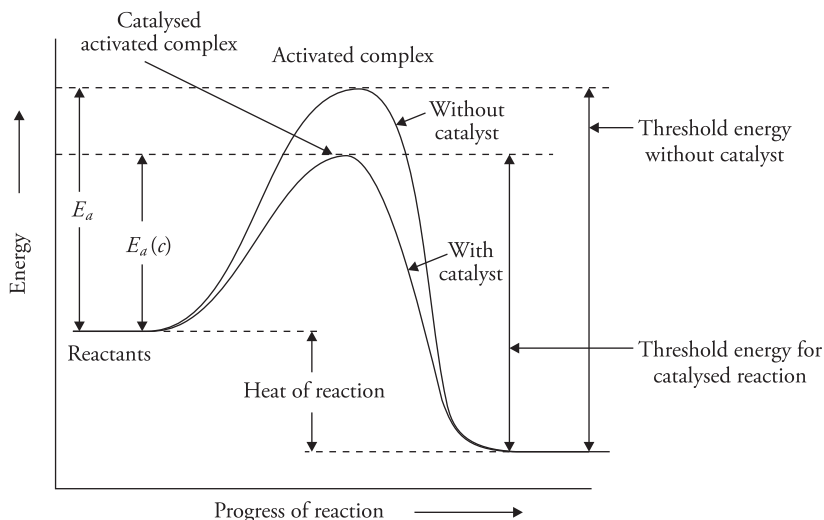
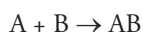


Figure 13.19 Comparison of activation energy in absence of a catalyst (E_a) and in the presence of a catalyst $E_a(c)$

Mechanism of homogeneous catalysis

Consider a homogeneous chemical reaction



The above reaction is catalysed by 'X'. According to the theory of homogeneous catalysis, the reaction proceeds as follows.

- (i) The catalyst first combines with the reactant to form an intermediate compound. This reactant with which the catalyst combines is generally termed as 'substrate'.



A is the substrate, X is the catalyst, AX is the intermediate compound and k_1 and k_2 are the velocity constants for the forward and backward reactions, respectively.

- (ii) The intermediate compound then reacts with the other reactant molecule B forming the product and the catalyst is regenerated.



The first step is fast and involves an equilibrium reaction, whereas the second step is slow. This step is the rate-determining step of the reaction.

$$\text{Rate of reaction} = k_3 [AX] [B] \quad (iii)$$

where k_3 is the velocity constant.

- (iii) The catalyst 'X' regenerated in the last step may further undergo steps (i) and (ii) to form more and more products. Thus, the rate of homogeneous catalytic reactions depends upon the concentration of the catalyst X and it is found that the rate of reaction increases with the increase in the concentration of the catalyst. This can be proved by studying the kinetics of the above reaction.

Kinetics of homogeneous catalytic reactions

As discussed above the rate of reaction is given by the equation:

$$\text{Rate of reaction} = k_3 [AX] [B] \quad (1)$$

The concentration of intermediate [AX] is found out by using the steady-state approximation, which states that the concentration of the intermediate does not change with time, that is,

The rate of formation of intermediate = Rate of its removal

$$\text{or} \quad \frac{d[AX]}{dt} = 0$$

$$\frac{d[AX]}{dt} = k_1[A][X] - k_2[AX] - k_3[AX][B] = 0$$

$$\text{or} \quad k_1[A][X] = k_2[AX] + k_3[AX][B]$$

$$\text{or} \quad [AX] = \frac{k_1[A][X]}{k_2 + k_3[B]} \quad (2)$$

Substituting the value of [AX] in Eq. (1), we get

$$\text{Rate of reaction} = \frac{k_1 k_3 [A][X][B]}{k_2 + k_3[B]} \quad (3)$$

Two cases may arise from Eq. (3)

- (i) If $k_2 \ll k_3[B]$ then the Eq. (3) becomes

$$\text{Rate of reaction} = \frac{k_1 k_3 [A][X][B]}{k_3[B]}$$

$$\text{Rate of reaction} = k_1[A][X] \quad (4)$$

- (ii) If $k_2 \gg k_3[B]$, then Eq. (3) becomes

$$\text{Rate of reaction} = \frac{k_1 k_3 [A][X][B]}{k_2} \quad (5)$$

Both Eq. (4) and (5) prove that the concentration of the catalyst affects the rate of reaction, although it is neither produced nor consumed in the reaction.

First	$-\frac{d[A]}{dt} = k_1[A]$	$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$	$t_{1/2} = \frac{0.693}{k_1}$	time ⁻¹ or s ⁻¹ , k is inde- pendent of initial concen- tration
Second	$-\frac{d[A]}{dt} = k_2[A]^2$	$k_2 = \frac{x}{at(a-x)}$	$t_{1/2} = \frac{1}{k_2 a}$	L mol ⁻¹ s ⁻¹
n th	$-\frac{d[A]}{dt} = k_n[A]^n$	$k_n = \frac{1}{(n-1)t} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$	$t_{1/2} = \frac{1}{(n-1)k_n a^{n-1}} (2^{n-1} - 1)$	L ⁿ⁻¹ mol ¹⁻ⁿ time ⁻¹ or (mol/L) ¹⁻ⁿ time ⁻¹

• **Examples of first-order reactions are as follows:**

- (i) $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ by titrating with KMnO_4 $a = V_0$; $a - x = V_t$

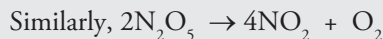
$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

- (ii) N-chloroacetanilide \rightarrow p-chloroacetanilide by adding KI and titrating with $\text{Na}_2\text{S}_2\text{O}_3$; KI reacts with N-chloroacetanilide $a = V_0$; $(a - x) = V_t$

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

- (iii) $\text{NH}_4\text{NO}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2$ The progress of the reaction is followed by measuring the volume of N_2

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$



The progress of the reaction is followed by measuring the volume of O_2 .

- (iv) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightleftharpoons{H^+} \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$

$$k = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t} \quad a = V_\infty - V_0; a - x = V_\infty - V_t$$

- (v) Inversion of cane sugar

$$k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty} \quad a = r_0 - r_\infty; x = r_0 - r_t; a - x = r_0 - r_\infty - r_0 + r_t = r_t - r_\infty;$$

r = angle of rotation



$$k = \frac{2.303}{t} \log \frac{r_\infty - r_0}{r_\infty - r_t} \quad p_t = \text{pressure of } \text{N}_2 \text{ at time } t;$$

p_∞ = pressure of N_2 on reaction completion;

p_0 = pressure at start of reaction.

(vii) Radioactive decay

$$k = \frac{2.303}{t} \log \frac{R_0}{R_t}$$

R_0 = initial activity

R_t = final activity

- Saponification (alkaline hydrolysis) of esters

$$k = \frac{x}{at(a-x)} = \frac{1}{t} \cdot \frac{V_0 - V_t}{V_0 V_t}$$

- **Method of rate determination**

(i) Hit and trial method substitute in integrated rate equation, calculate k

(ii) Fractional change method.

$$t \propto \frac{1}{a^{n-1}}$$

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2} \right)^{n-1} \quad \text{or} \quad n = 1 + \frac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$$

(iii) Van't Hoff differential method.

$$-\frac{dc}{dt} = kc^n$$

$$\text{or} \left(\frac{c_1}{c_2} \right)^n = \frac{-dc_1 / dt(\text{rate}_1)}{-dc_2 / dt(\text{rate}_2)}$$

$$\log \left[-\frac{dc_1}{dt} \right] - \log \left[-\frac{dc_2}{dt} \right] = n \log(c_1 - c_2)$$

$$n = \frac{\log \left[-\frac{dc_1}{dt} \right] - \log \left[-\frac{dc_2}{dt} \right]}{\log c_1 - \log c_2}$$

(iv) Ostwald's isolation method



Rate of the reaction

$$\frac{dx}{dt} = k c_A^p \cdot c_B^q \cdot c_C^r$$

$$\text{Total order} = p + q + r$$

(v) Varying ratio by definite fraction

$$\text{rate} \propto k[A]^p[B]^q$$

Calculate ratio of 2 rates and hence p and q

$$\text{order} = p + q$$

- Arrhenius equation $\log k = \log A - \frac{E_a}{2.303RT}$

- Collision theory $k = p \frac{z_{AA}}{n_A^2} e^{-E/RT}$ (4)

$$z_{AA} = \frac{1}{2} \left(\pi \sigma_{AA}^2 \right) \left(\frac{16kT}{\pi m_A} \right)^{1/2} n_A^2$$

Transition state theory

$$\text{or } k = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

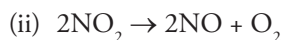
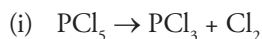
Review Questions

- Define the following:
 - Chemical kinetics
 - Rate of reaction
 - Order of a reaction
 - Molecularity
 - Average rate and instantaneous rate
- What is a rate law expression? Differentiate between rate of reaction and rate constant.
- What are rate constants? What are the units of rate constants for zero-order, first-order and second-order reactions?
- Define the rate of a reaction. Discuss the various factors affecting reaction rates.

5. How can you derive the rate law expression for a multi-step chemical reaction? Explain taking a suitable example.
6. Define and explain order and molecularity of a reaction giving suitable examples. Differentiate between order and molecularity of a reaction.
7. What is a pseudo-unimolecular reaction? Explain with the help of a suitable example.
8. Derive the integrated rate equation for a first-order reaction. What are the units of rate constant for this reaction?
9. Define half-life of a reaction. Derive the expression for half-life of a second-order reaction.
10. What is rate-determining step? Show that the slowest step in the mechanism of a reaction determines the rate of the reaction.
11. What do you understand by order of a chemical reaction? The reaction $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$ has been found to be of first order with respect to NO_2 and with respect to F_2 .
 - (i) Write the rate law expression
 - (ii) What is the overall order of the reaction
 - (iii) Suggest a suitable mechanism for the reaction.
12. Derive the integrated rate equation for a second-order reaction when
 - (a) $2\text{A} \rightarrow \text{Products}$
 - (b) $\text{A} + \text{B} \rightarrow \text{Products}$
13. How can you find the order of a reaction by initial rate method?
14. Explain the variation of rate of a reaction with temperature. Derive the Arrhenius equation for temperature dependence of reaction rates.
15. How can order of reaction be found out by the following?
 - (i) Integrated equation method
 - (ii) Fractional change method
 - (iii) Van't Hoff differential method
 - (iv) Ostwald's isolation method
16. What is the collision theory of reaction rates?
17. What are the main features of the Absolute reaction rate theory or transition state theory?
18. Define the rate of a reaction. For the reaction $\text{A} \rightarrow \text{B}$, the rate of the reaction can be denoted by $-\frac{d[\text{A}]}{dt}$ or $+\frac{d[\text{B}]}{dt}$. Explain the significance of the plus and minus signs in these expressions.
19. What is energy of activation of a reaction? How does a catalyst affect the activation energy?
20. How does Arrhenius equation help in calculating the activation energy?
21. What is a catalyst? Explain homogeneous and heterogeneous catalysis processes with the help of suitable examples.
22. Explain the characteristics of a catalyst.
23. Discuss the mechanism and kinetics of homogeneous catalysis.
24. What is the potential energy of surfaces. Explain the potential energy surface for H_3 surface.
25. Explain the potential energy surfaces of H_2F and HCN . Also explain the trajectories on these surfaces.

Additional Problems

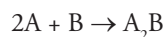
1. Express the rate of the following reactions in terms of concentration of reactants and products.



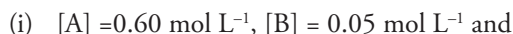
$$[\text{Ans (i)}] \quad -\frac{d[\text{PCl}_5]}{dt} = \frac{d[\text{PCl}_3]}{dt} = \frac{d[\text{Cl}_2]}{dt}$$

$$[\text{Ans (ii)}] \quad -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

2. The rate of a reaction

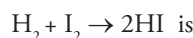


has a rate law $\text{rate} = k[\text{A}]^2$ with rate constant equal to $0.50 \text{ mol}^{-1} \text{ L s}^{-1}$. Calculate the rate of the reaction when



3. A reaction is 50% complete in 16 min. What fraction of the reaction would occur in 32 min. [Ans 75%]

4. The specific rate constant for the reaction



$2.34 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ at 673 K and $7.50 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ at 773 K. Calculate the activation energy for the reaction. [Ans $E_a = 149.99 \text{ kJ mol}^{-1}$]

5. The rate of a particular reaction quadruples when the temperature changes from 293 to 313 K. Find the energy of activation for the reaction. [Ans $E_a = 52.858 \text{ kJ}$]

6. Hydrogen peroxide decomposes into water and oxygen. The concentration of H_2O_2 was determined by titrating the reaction mixture against standard KMnO_4 solution. The following data were obtained:

Time (min)	0	10	20	30	40	50
Conc. of H_2O_2	0.1297	0.1162	0.1045	0.0940	0.0845	0.0760

Prove that it is a first-order reaction and calculate the rate constant

$$[\text{Ans } k = 0.01078/\text{min}]$$

7. The following mechanism has been suggested for the thermal decomposition of ozone:



Show that the overall rate of the reaction is given by

$$-\frac{d[\text{O}_3]}{dt} = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

assuming that $k_{-1}[\text{O}_2] \gg k_2[\text{O}_3]$

Solution

The step II is a rate-determining step. Hence,

$$-\frac{d[\text{O}_3]}{dt} = k_2[\text{O}_3][\text{O}] \quad (\text{i})$$

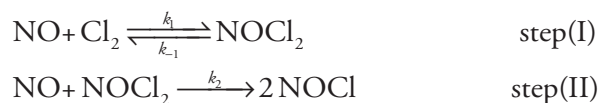
Applying steady-state approximation to concentration of atomic oxygen [O], we get:

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= 0 = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}_3][\text{O}] \\ \text{or } k_1[\text{O}_3] &= k_{-1}[\text{O}_2][\text{O}] + k_2[\text{O}_3][\text{O}] \\ \text{or } k_1[\text{O}_3] &= [\text{O}]\{k_{-1}[\text{O}_2] + k_2[\text{O}_3]\} \\ [\text{O}] &= \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \quad (\text{ii}) \end{aligned}$$

Placing the value of [O] in Eq. (i) we have

$$\begin{aligned} -\frac{d[\text{O}_3]}{dt} &= k_2[\text{O}_3] \cdot \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \\ &= \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1}[\text{O}_2] + k_2[\text{O}_3]} \\ &= \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1}[\text{O}_2]} \quad \text{Since } k_{-1}[\text{O}_2] \gg k_2[\text{O}_3] \\ &= \frac{k[\text{O}_3]^2}{[\text{O}_2]} \quad \text{where } k = \frac{k_1 k_2}{k_{-1}} \end{aligned}$$

8. For the reaction $2\text{NO} + \text{Cl}_2 \rightleftharpoons 2\text{NOCl}$, the following mechanism has been proposed:



Show that the overall rate of the reaction is $k[\text{NO}]^2[\text{Cl}_2]$ where $k = \frac{k_1 k_2}{k_{-1}}$ assuming that $k_{-1} \gg k_2[\text{NO}]$

Solution

The overall rate of reaction is given by

$$-\frac{d[\text{NOCl}]}{dt} = k_2[\text{NO}][\text{NOCl}_2] \quad (\text{i})$$

Applying steady-state approximation to the concentration of NOCl_2 , we get

$$\begin{aligned} \frac{d[\text{NOCl}_2]}{dt} = 0 &= k_1[\text{NO}][\text{Cl}_2] - k_{-1}[\text{NOCl}_2] - k_2[\text{NO}][\text{NOCl}_2] \\ \therefore [\text{NOCl}_2] &= \frac{k_1[\text{NO}][\text{Cl}_2]}{k_{-1} + k_2[\text{NO}]} \quad (\text{ii}) \end{aligned}$$

From Eq. (ii) putting the value of $[\text{NOCl}_2]$ in Eq. (i), we get

$$\begin{aligned} -\frac{d[\text{NOCl}]}{dt} &= \frac{k_1 k_2 [\text{NO}][\text{NO}][\text{Cl}_2]}{k_{-1} + k_2[\text{NO}]} \\ &= \frac{k_1 k_2 [\text{NO}]^2 [\text{Cl}_2]}{k_{-1} + k_2[\text{NO}]} \quad \text{now since } k_{-1} \gg k_2[\text{NO}] \\ &= \frac{k_1 k_2 [\text{NO}]^2 [\text{Cl}_2]}{k_{-1}} = k[\text{NO}]^2 [\text{Cl}_2] \quad \text{where } k = \frac{k_1 k_2}{k_{-1}} \end{aligned}$$

9. The following values for the first-order rate constant were obtained for a certain reaction

Temperature °C	k (s ⁻¹)
25	3.46×10^{-5}
65	4.87×10^{-3}

Calculate the energy of activation and Arrhenius frequency factor

$$[\text{Ans } E_a = 103.564 \text{ kJ}; A = 4.894 \times 10^{13}]$$

10. The optical rotation of sucrose in 0.5 N HCl at 35 °C and at various time intervals are given below. Find out the order of the reaction.

Time (min)	0	10	20	30	40	∞
Rotation (degree)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1.

[Ans first order]

11. The half-life was found to be 30 min when the initial concentration was 0.1. Determine the rate constant when the reaction is of second order.

$$[\text{Ans } 0.333 \text{ mol L}^{-1} \text{ min}^{-1}]$$

12. A radioactive compound decomposes according to the first-order rate law with a half-life period of 50 min. What fraction of a sample remains after 100 min of reaction. [Ans 0.25]

Multiple Choice Questions

- Which of the reaction will be the fastest
 - Rusting of iron
 - Burning of coal
 - Inversion of cane sugar
 - Precipitation of AgCl by mixing AgNO₃ and NaCl solution
- The instantaneous rate for the reaction $2X + Y \rightarrow X_2Y$ can be expressed as
 - $-\frac{d[X]}{dt}$
 - $-\frac{1}{2} \frac{d[X]}{dt} \cdot \frac{d[Y]}{dt}$
 - $-\frac{1}{2} \frac{d[X]}{dt}$
 - $\frac{1}{2} \frac{d[X_2Y]}{dt}$
- Molecularity of a chemical reaction is
 - Always a whole number
 - Cannot be less than 2
 - Can have a fractional number
 - Can be zero
- The rate constant of a reaction depends on
 - Temperature
 - Mass
 - Time
 - Weight
- In a first-order reaction when $A \rightarrow \text{product}$, a is the initial concentration, $(a - x)$ is the concentration of reactants after time t , then the rate constant k is given by
 - $k = \frac{2.303}{t} \log \frac{a-x}{a}$
 - $k = \frac{2.303}{t} \log \frac{a}{a-x}$
 - $k = t \log \frac{a}{a-x}$
 - $k = \frac{t}{2.303} \log \frac{a}{a-x}$
- The increase in the rate of reaction with the increase in temperature is due to
 - Lowering of activation energy
 - Increase in the number of collisions
 - Increase in the number of effective collisions
 - Shortening of the mean free path
- Which of the following is a zero-order reaction
 - Photochemical combination of H₂ and Cl₂
 - Decomposition of N₂O₅
 - Radioactive decay
 - Reaction between hydrogen and bromine to form HBr

8. If 'a' is the initial concentration of reactants, then the half-life of a second-order reaction is

(a) $t_{1/2} = \frac{0.693}{k_2}$

(b) $t_{1/2} = \frac{1}{k_2 a}$

(c) $t_{1/2} = k_2 a$

(d) $t_{1/2} = \frac{a}{k_2}$

9. The dimension of rate of a reaction are

(a) Mol liter⁻¹

(b) Mol liter s⁻¹

(c) Mol liter⁻¹ s⁻¹

(d) Mol⁻¹ liter⁻² s⁻¹

10. The specific reaction rate for a reaction is 1.0×10^{-4} mol L⁻¹ min⁻¹. The order of the reaction is

(a) Zero

(b) One

(c) Two

(d) Three

11. Which of the following expressions represents the expression for $\frac{3}{4}$ life of a reaction:

(a) $\frac{k}{2.303} \log \frac{4}{3}$

(b) $\frac{2.303}{k} \log \frac{4}{3}$

(c) $\frac{2.303}{k} \log 4$

(d) $\frac{2.303}{k} \log 3$

12. Consider a reaction $A + 2B \rightarrow \text{Products}$, The rate of reaction is given by $-\frac{d[A]}{dt} = k[A][B]^2$. If B is present in large excess, the order of the reaction is

(a) 3

(b) 2

(c) 1

(d) 0

13. If 75% of a radioactive element disintegrates in 60 minutes, the half-life of the radio element is

(a) 20 min

(b) 30 min

(c) 45 min

(d) 25 min

14. The rate equation for a second-order reaction is given by

(a) $k = \frac{2.303}{t} \log \frac{a}{a-x}$

(b) $k = \frac{1}{t} \log \frac{a}{a-x}$

(c) $k = \frac{1}{t} \log \frac{a^2}{a-x}$

(d) $k = \frac{1}{t} \times \frac{x}{a(a-x)}$

15. Consider a reaction $A + B \rightarrow \text{Products}$. When the initial concentration of A is doubled the reaction increases four times while on doubling the concentration of B the rate increases two times, the overall order of the reaction is

- (a) 1 (b) 2
(c) 3 (d) 0
16. According to collision theory, the rate of reaction is equal to
(a) Total number of collisions (b) Number of effective collisions
(c) Concentration of reactants (d) Concentration of products.
17. The rate constant k according to collision theory is given by
(a) $k = ze^{-\frac{E_a}{RT}}$ (b) $k = ze^{-\frac{E_a}{RT^2}}$
(c) $k = Pze^{-\frac{E_a}{RT}}$ (d) $k = Pze^{-\frac{E_a}{RT^2}}$
18. According to the transition state theory (also called the theory of absolute reaction rates) rate of any reaction is given by
(a) Rate of formation of products (b) Rate of decomposition of activated complex
(c) Rate of decomposition of reactants (d) Rate of formation of activated complex
19. The value of k according to transition state theory is
(a) $k = \frac{RT}{Nh} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}}$ (b) $k = \frac{RT}{N} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}}$
(c) $k = \frac{RT}{Nh} e^{\frac{\Delta S^\ddagger}{RT}} e^{\frac{-\Delta H^\ddagger}{RT}}$ (d) $k = \frac{RT^2}{Nh} e^{\frac{\Delta S^\ddagger}{R}} e^{\frac{-\Delta H^\ddagger}{RT}}$
20. The expression $(k_{t+10}) / k_t$ is known as
(a) Temperature coefficient (b) Equilibrium constant
(c) Temperature ratio (d) None of the above
21. Arrhenius equation can be written as
(a) $\frac{d \ln k}{dt} = \frac{-\Delta E^0}{RT}$ (b) $\frac{d \ln k}{dt} = \frac{\Delta E^0}{RT^2}$
(c) $\frac{d \ln k}{dt} = \frac{-\Delta E^0}{RT^2}$ (d) $\frac{d \ln k}{dt} = \frac{-\Delta E^0}{R^2 T}$
22. In homogenous catalysis
(a) The reactants, products and catalyst are in the same phase
(b) The reactant and catalyst are in the same phase but products are in different phase
(c) The product and catalyst are in the same phase but the reactants are in different phase
(d) The reactants, products and catalyst all are in different phases.

23. The rate constant of a first order reaction is $2 \times 10^{-2} \text{ min}^{-1}$. Its half-life period is
- (a) $\frac{2.303}{2 \times 10^{-2}} \text{ min}$ (b) $\frac{2 \times 10^{-2}}{2.303} \text{ min}$
(c) 34.65 min (d) 69.3 second
24. For most reactions, an increase in temperature from 300 K to 310 K increases the rate approximately by
- (a) 3.3% (b) 100%
(c) 10% (d) 1000%
25. Which of the following potential energy surface does not have a saddle point
- (a) H_3 (b) H_2F
(c) $\text{HC} + \text{N}$ (d) None of the above

Solution

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (d) | 2 (c) | 3 (a) | 4 (a) | 5 (b) | 6 (c) | 7 (a) | 8 (b) |
| 9 (c) | 10 (a) | 11 (c) | 12 (c) | 13 (b) | 14 (d) | 15 (c) | 16 (b) |
| 17 (c) | 18 (b) | 19 (a) | 20 (a) | 21 (b) | 22 (a) | 23 (c) | 24 (b) |
| 25 (c) | | | | | | | |

Chapter 14

SURFACE CHEMISTRY

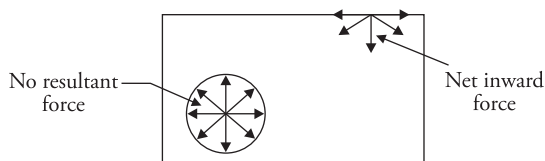
14.1 Introduction

Various physical and chemical reactions occur at the interfaces or boundaries of two different phases like solid–liquid interface, solid–solid interface, solid–gas interface, liquid–gas interface, liquid–solid interface and liquid–liquid interface. These reactions have been of great interest to the chemists worldwide as they have important applications in industrial and domestic field.

All these changes occurring at the boundaries of different phases are studied under a branch of chemistry called surface chemistry. Surface chemistry not only deals with the reactions occurring at the interfaces but also studies the nature of surfaces and the reactions taking place at the surfaces. Adsorption and colloidal properties are some of the important effects that occur at the solid – liquid interfaces.

14.2 Adsorption

The surface of solid or liquid has a tendency to attract and retain molecules of other species (gas or liquids). This phenomenon of attracting and retaining molecules on the surface is termed as adsorption (*latin word surbere; to suck up*). The material on the surface of which adsorption occurs is termed as *adsorbent* and the substance adsorbed on the surface is called *adsorbate*. Now, the question of why adsorption occurs arises. Adsorption occurs because of the presence of unbalanced forces at the surface of liquids and solids. In a solid or liquid, the molecules present in the bulk are attracted equally from all sides and the net force experienced by the molecule in the bulk is zero. However, the molecule that lies near the surface (known as surface molecule) is being attracted only by the molecules below it because there are no molecules above it (Fig. 14.1). Hence, a net downward force is experienced by the surface molecule. Because of this downward force, the surface molecule tends to attract and retain other species (a gas or a dissolved substance). These species do not penetrate inside the molecule but remain on the surface. Hence, their concentration is higher on the surface than in the bulk.

**Figure 14.1** *Forces in a liquid or a solid substance*

Common examples of adsorption are

- (i) Finely divided activated charcoal adsorbs a number of gases like ammonia, sulphur dioxide, chlorine, etc.
- (ii) Animal charcoal adsorbs dyes and is used for decolorising a number of organic substances.

Absorption

Unlike adsorption where the adsorbed molecules remain on the surface, in absorption, the atoms or molecules enter inside the bulky material and are incorporated into the absorbent. They cannot be easily separated from the absorbent. For example, ammonia is adsorbed by charcoal but it is absorbed by water to form ammonium hydroxide.

Difference between adsorption and absorption

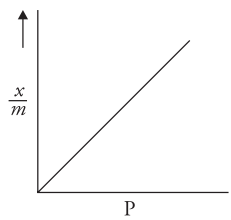
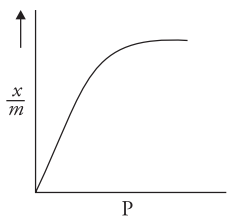
The terms adsorption and absorption are different. Adsorption is a surface phenomenon in which the concentration of molecules is higher on the surface than in the bulk. On the other hand, in the phenomenon of absorption the molecule penetrates inside; hence, the concentration of the absorbed molecules is the same in the bulk and on the surface. For example, when silica gel is placed in a moist environment it adsorbs the water vapor. The concentration of water vapor is higher at the surface. On the other hand, when calcium chloride is placed in moist environment, it absorbs water. The water gets uniformly distributed throughout the body of calcium chloride. Thus, silica gel adsorbs moisture and calcium chloride absorbs moisture.

Thus, adsorption is a surface phenomenon, whereas absorption is a bulk property.

Table 14.1 gives important points of distinction between adsorption and absorption.

Table 14.1 Difference between adsorption and absorption

S. No	Absorption	Adsorption
1.	The distribution of particles inside the bulk of the solid or liquid is uniform	Since the gas or liquid particles do not enter inside the bulk, their concentration at the surface is higher
2.	It is a bulk phenomenon	It is a surface phenomenon
3.	Absorption occurs at a uniform rate	Adsorption is rapid in the beginning and its rate slowly decreases
4.	Endothermic process	Exothermic process
5.	Attainment of equilibrium takes time	Equilibrium is easily attained
6.	There is no direct relation between rate of absorption and surface area	It depends on surface area. Larger the surface area, faster is the rate of adsorption

7.	 <p>Absorption Isotherm</p>	 <p>Adsorption Isotherm</p>
8.	Example includes absorption of water vapor by calcium chloride	Example includes adsorption of water vapor by silica gel

Sorption

In this process adsorption and absorption occur simultaneously. The substance first gets adsorbed on the surface and then gradually penetrates inside and is uniformly distributed in the bulk.

Common examples of sorption are as follows:

- Uptakes of gases by zeolites.
- When hydrogen is taken up by charcoal, first it is adsorbed on the surface. Gradually it diffuses inside the surface. Therefore, the hydrogen gas is adsorbed as well as absorbed by charcoal.

When gases are adsorbed on metal, the phenomenon is specifically termed as occlusion.

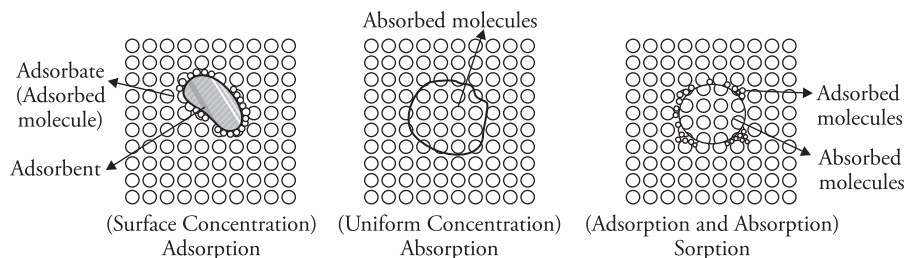


Figure 14.2 Illustration of adsorption, absorption and sorption

14.3 Factors Affecting Adsorption

The phenomenon of adsorption of gases by solids depends on the following factors:

(i) Nature of adsorbate and adsorbent

- It has been found that gases that are easily liquifiable (like CO_2 , NH_3 , Cl_2 and SO_2) are more easily adsorbed than permanent gases like H_2 , N_2 , O_2 and He that do not liquify easily. This is because easily liquifiable gases have greater van der Waals forces or they have greater forces of attraction.
- Nature of adsorbate also has an important role in adsorption. Charcoal and fullers earth adsorb fast as they are porous and finely powdered solids. Hard and non-porous materials adsorb slowly.

- (ii) **Surface area of the adsorbent** As adsorption is a surface phenomenon, larger the surface area, greater is the extent of adsorption.
- (iii) **Effect of partial pressure of the adsorbate gas** The extent of adsorption of a gas per unit mass of the adsorbent depends upon the pressure of the gas. A plot of the amount of adsorption and gas pressure keeping the temperature constant is called the *adsorption isotherm* (Fig. 14.3). It has been found that the extent of adsorption (expressed as x/m , where x is the mass of adsorbate and m is the mass of the adsorbent) increases with pressure and becomes maximum corresponding to pressure P_s , called the equilibrium pressure. As adsorption is a reversible process, adsorption and desorption occurs simultaneously. At this pressure P_s , the amount of gas adsorbed becomes equal to the amount of gas desorbed. Therefore, further increase in pressure does not alter the extent of adsorption. This state of maximum adsorption is called the saturation state and the corresponding pressure is the saturation pressure (P_s).

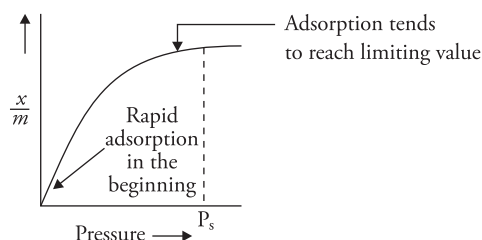


Figure 14.3 Adsorption isotherm

- (iv) **Effect of temperature** Adsorption is an exothermic process; hence, according to Le Chatelier's principle, increase in temperature will decrease the extent of adsorption. The graph between the extent of adsorption and temperature at constant pressure is called *adsorption isobar*. This is true for physical adsorption only (Fig. 14.4). However, in chemical adsorption, the adsorption first increases and then decreases with the rise in temperature. This is because like all chemical reactions, some activation energy is required for chemisorption. At low temperature x/m is small but as the temperature rises the molecules gain energy equal to their activation energy and form bonds with the adsorbent molecules. Therefore, the amount of gas adsorbed increases with the rise in temperature. The kinetic energy of the adsorbed molecules increases as the temperature is further increased. This increases the rate of desorption and therefore decreases the extent of adsorption.

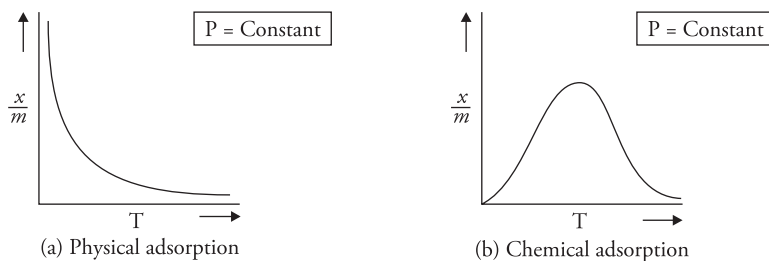


Figure 14.4 Adsorption isobar

- (v) **Activation of adsorbent** The adsorbing power of adsorbent is increased by activation. This can be done by
- Mechanical rubbing or chemical treatment for metallic adsorbents.
 - Subdividing the adsorbent: This increases the surface area and hence the adsorbing power.
 - Activating by strong heating in superheated steam: For example, charcoal is activated by subjecting it to the action of superheated steam. It opens the pores, thereby increasing the rate of adsorption.

14.4 Types of Adsorption

Depending upon the nature of forces that hold the molecules of the adsorbate on the surface of the adsorbent, there are two types of adsorption: (i) physical adsorption and (ii) chemical adsorption.

Physical adsorption (physisorption)

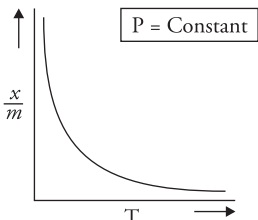
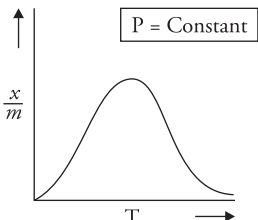
In physical adsorption, physical forces hold the adsorbate particles to the surface of the adsorbent. These forces are van der Waals forces, permanent dipole moment in adsorbed molecule, polarisation effects, dispersion effects, etc. These forces are weak forces. The heat of adsorption in this type is on the order of 20–40 kJ/mol. As the adsorbate molecules are held by weak forces, they leave the surface of the adsorbent as the temperature is increased because of increase in their kinetic energy. Therefore, by increasing the temperature or by decreasing the pressure, physical adsorption can be easily reversed. Moreover, physical adsorption does not depend on the chemical nature of the substance that is adsorbed.

Chemical adsorption (chemisorption)

In chemical adsorption, chemical forces bind the adsorbate particles to the surface of the adsorbent. This type of adsorption is irreversible and takes place by strong chemical interaction between the adsorbed molecules and the adsorbent surface. The heat of adsorption is on the order of 200–400 kJ/mol. Unlike physical adsorption, this is highly specific and takes place at high temperature and is also known as *activated adsorption*.

Table 14.2 Difference between physical adsorption and chemical adsorption

S.No.	Physical adsorption	Chemical adsorption
1	Weak physical forces like van der Waals forces hold the adsorbate molecules and the adsorbent particles together. No bond formation occurs between the adsorbate and the adsorbent	Strong chemical forces hold the adsorbate molecules and the adsorbent particles together. There is bond formation between the adsorbate and the adsorbent
2	Heat of adsorption is low, on the order of 20–40 kJ/mol	Heat of adsorption is high, on the order of 200–400 kJ/mol

3	It occurs at low temperature. Extent of adsorption decreases with rise in temperature	It occurs at high temperature
4	Extent of physical adsorption increases with the rise in pressure	Rate of chemisorption decreases with increase in pressure
5	It is reversible	It is irreversible
6	Easily liquefiable gases like CO_2 , NH_3 , Cl_2 , etc. have greater van der Waals forces, hence extent of physical adsorption in such gases is high	As this adsorption involves bond formation, the extent of adsorption does not depend upon the ease of liquefaction of the gas
7	As this adsorption involves only physical forces, it is not specific in nature and the solid adsorbs all gases to the same extent	As this adsorption involves bond formation between the adsorbate and the adsorbent, it is highly specific in nature
8	Multimolecular layers are formed	Only a monolayer is formed
9	No surface compound is formed. The state of adsorbate does not change after adsorption. It is the same as in the bulk	Surface compounds are formed and the state of adsorbate on the surface may be different from that in the bulk. New compound may be formed
10	It is an instantaneous process	It may be rapid or slow
11	As adsorption is a physical phenomenon, activation energy is not required	As a chemical process (bond formation) occurs, activation energy is required
12	Physical adsorption shows a decrease in $\frac{x}{m}$ along the rise in temperature	Chemisorption adsorption isobar shows an initial increase in adsorption with temperature and then there is unexpected decrease
	 <p>A graph showing the variation of $\frac{x}{m}$ (y-axis) with temperature T (x-axis) for physical adsorption at constant pressure P. The curve starts at a high value of $\frac{x}{m}$ at low T and decreases rapidly, then levels off as T increases. A box labeled 'P = Constant' is present in the upper right of the graph area.</p>	 <p>A graph showing the variation of $\frac{x}{m}$ (y-axis) with temperature T (x-axis) for chemisorption at constant pressure P. The curve starts at the origin, rises to a peak, and then decreases. A box labeled 'P = Constant' is present in the upper right of the graph area.</p>

14.5 Type of Adsorption Isotherms

The various types of adsorption isotherms are as follows.

Freundlich Adsorption Isotherm

In 1909, Freundlich proposed an empirical equation for expressing the variation of adsorption of a gas with pressure at constant temperature. He proposed that

$$\frac{x}{m} = kp^{1/n} \quad (1)$$

where

x is the amount of adsorbate

m is the amount of adsorbent

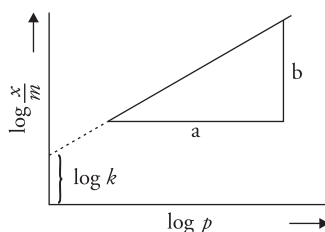
p is the pressure

k and n are two constants that depend upon the nature of adsorbent and adsorbate, and n being less than unity.

On taking log of both sides, Eq. (1) becomes

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \quad (2)$$

If $\log \frac{x}{m}$ is plotted against $\log p$, a straight line should be obtained as shown in Figure 14.5. The slope of the line gives the value of $1/n$ and the intercept on y -axis gives the value of $\log k$.



Intercept = $\log k$; slope = $b/a = 1/n$

Figure 14.5 Plot of $\log x/m$ v/s $\log p$

Analysis of the above graph shows that as p increases $\frac{x}{m}$ also increases. Hence, the adsorption would increase to an unlimited extent with the increase in pressure; however, experimentally deviations are observed. The Freundlich adsorption isotherm could explain the adsorption of gases at low pressure but it could not explain the adsorption phenomenon at high pressure. The curve obtained experimentally is shown in Figure 14.6.

Graph $\frac{x}{m}$ v/s pressure.

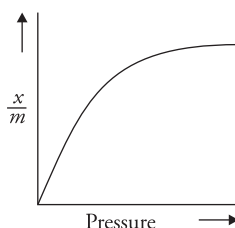


Figure 14.6 Plot of x/m v/s pressure

The above graph shows that

- (i) *At low pressure*, the graph is almost a straight line indicating $x/m \propto p$ or $x/m = kp$
- (ii) *At high pressure*, the graph becomes almost parallel to the x -axis, which means that x/m becomes independent of pressure. This can be written as

$$\frac{x}{m} = \text{constant} \quad \text{or} \quad \frac{x}{m} \propto p^0 \quad \text{or} \quad \frac{x}{m} = kp^0$$

- (iii) *At intermediate pressure*, x/m will depend upon the power of pressure that lies between 0 and 1, that is, fractional power of pressure. This can be expressed as

$$\frac{x}{m} \propto p^{1/n} \quad \text{or} \quad \frac{x}{m} = kp^{1/n}$$

where n can take any whole number value depending upon the nature of adsorbate and adsorbent.

Limitations of Freundlich equation

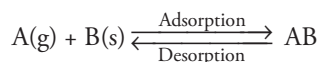
- It is purely empirical formula without any theoretical basis.
- It holds good over a certain range of pressure only. It does not apply to adsorption of gases by solids at high pressures.
- The constant k and n vary with temperature.

Langmuir Adsorption Isotherm

To overcome the limitations of the Freundlich equation, Irving Langmuir in 1916 worked out a new adsorption isotherm for gases adsorbed on solids. It is based on four assumptions

- (i) Langmuir considered the formation of a unimolecular layer of the adsorbate on the adsorbent. Although at pressure approaching the saturation value (high pressure) multi-molecular layer of the adsorbed molecules is possible, he considered only unimolecular layer while deriving this relation.
- (ii) Adsorption occurs at fixed sites and the adsorbed molecules do not interact. One site adsorbs one molecule. Hence, when the entire surface of the adsorbent is covered by a unimolecular layer of the gas, further adsorption is not possible and saturation is reached.
- (iii) Adsorption is a dynamic process. It involves simultaneous adsorption and desorption of the gas molecules from the surface of the solid.

Langmuir suggested the following mechanism for adsorption



where

$A(g)$ = gaseous adsorbate molecules

$B(s)$ = solid adsorbent

AB = metal surface after adsorption of gas molecules.

On the basis of the above postulates, Langmuir deduced a quantitative relationship between the amount of gas adsorbed at a particular pressure at constant temperature.

Derivation Consider a surface on which the molecules of a gas are condensing and evaporating. Let,

θ = fraction of total surface covered by the gas molecules at a particular instance.

If 1 cm^2 is the total surface area, then

$1 - \theta$ = fraction of the surface area that is bare

Rate of adsorption will be proportional to the bare area

Rate of adsorption $r_1 = k_1(1 - \theta)p$

k_1 = specific adsorption constant and

p = pressure of the overlying gas

Similarly,

Rate of desorption (r_2) \propto Fraction of the surface covered
 $= k_2 \theta$

k_2 = specific desorption rate constant

At equilibrium,

$$r_1 = r_2$$

$$k_1(1 - \theta)p = k_2\theta \quad (1)$$

$$\text{or } \theta = \frac{k_1 p}{k_2 + k_1 p}$$

Dividing the numerator and denominator by k_2 , we get

$$\theta = \frac{\frac{k_1}{k_2} p}{1 + \frac{k_1}{k_2} p} = \frac{kp}{1 + kp} \quad (2)$$

$$\text{where } k = \frac{k_1}{k_2}$$

where k is the equilibrium constant and is referred to as the adsorption coefficient.

However, the quantity of gas adsorbed per unit mass of the adsorbent $\frac{x}{m}$ is proportional to the surface covered, that is

$$\frac{x}{m} \propto \theta \quad (3)$$

$$\text{or } \frac{x}{m} = K\theta \quad (4)$$

where K is another proportionality constant. Equation (3) implies that the amount of gas adsorbed per unit mass of the adsorbent is proportional to the fraction of the surface covered. Substituting the value of θ from Eq. (2) we get

$$\frac{x}{m} = \frac{Kkp}{1 + kp} \quad (5)$$

$$\text{or } \frac{1}{x/m} = \frac{1 + kp}{Kkp} \quad \text{or } \frac{p}{x/m} = \frac{1}{Kk} + \frac{p}{K} \quad (6)$$

Equation (6) is known as the Langmuir adsorption isotherm. A plot of $\frac{p}{x/m}$ against p should be a straight line. Langmuir adsorption isotherm holds good at all the pressures. Let us discuss it one by one.

Case I – At low pressure At very low pressure, kp of Eq. (5) becomes negligible in comparison with unity. The equation thus reduces to

$$\frac{x}{m} = Kkp \quad \text{or } \frac{x}{m} \propto p$$

Thus, at low pressure, the amount of gas adsorbed per unit quantity of the adsorbent is directly proportional to the pressure. This has been confirmed experimentally.

Case II – At high pressure kp becomes larger than unity, hence ignoring '1' in denominator Eq. (5) becomes

$$\frac{x}{m} = \frac{Kkp}{kp} \quad \text{or } \frac{x}{m} \propto K$$

This equation shows that at high pressure adsorption is independent of pressure because the surface becomes completely covered.

Case III – At moderate pressure

As studied earlier at low pressure

$$\frac{x}{m} = \text{constant} \times p$$

and at high pressure $\frac{x}{m} = \text{constant}$ or $\frac{x}{m} = \text{constant} \times p^0$

Hence, at moderate pressure an expression of the type

$$\frac{x}{m} = \text{constant} \times p^{1/n}$$

where $1/n$ lies between 0 and 1 may be expected to hold good.

(n = number of molecules of the gas striking 1 cm^2 of the surface area per second).

14.6 Applications of Adsorption

The adsorption phenomenon has various important applications. Some of them are as follows

1. *In gas masks* The gas masks use activated charcoal that adsorbs the toxic gases from the atmosphere and purifies the air. These masks are commonly used by miners because poisonous gases like CO, CH_4 , etc. are common in the atmosphere of the mines. These masks help to purify the air for breathing.
2. *Removal of coloring matter from sugar juice and vegetable oils* Activated animal charcoal is used to decolorise sugar solution and vegetable oils.
3. *Dyeing of cloth* Mordants such as alum are used in dyeing of clothes. They adsorb the dye particles that do not otherwise stick to the cloth.
4. *For dehumidification* Silica gel is commonly used to adsorb moisture from air. It is used for controlling humidity and for storing delicate instruments, which may otherwise be damaged by moisture.
5. *Heterogeneous catalysis* Most of the heterogeneous catalysis reactions proceed by adsorption of the gaseous reactants on the solid catalyst. For example,
 - Finely divided Ni is used for the hydrogenation of oils.
 - Finely divided Fe obtained by reducing Fe_3O_4 (magnetite) is used in Haber's process for the manufacturing of ammonia.
 - Vanadium pentoxide (V_2O_5) is used in the manufacture of sulphuric acid by contact process.
6. *For water softening* Organic polymers containing $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{NH}_2$ groups soften water by selectively adsorbing the ions from solutions.
7. *As adsorption indicators* Many dyes can be used as indicators in volumetric analysis owing to their adsorption properties. For example, dyes such as eosin and fluorescein are used as adsorption indicators.
8. *In qualitative analysis* Qualitative tests for Al^{3+} ions like lake test are based on the adsorption of color of litmus by $\text{Al}(\text{OH})_3$.
9. *In chromatography* Adsorption chromatography, paper chromatography and vapor phase chromatography are all based on selective adsorption of different substances on the adsorbent. It is used to separate and purify hormones, pigments, etc.
10. *Drugs* The germicidal action of medicines is based on the property of adsorption.

11. *Production of high vacuum* Activated charcoal is used in Dewar flask to create vacuum. Finely divided coconut charcoal adsorbs all gases and creates vacuum. Silica gel is also used as an adsorbent to produce high vacuum.
12. *Separation of inert gases* Adsorption on coconut charcoal can be used to separate a mixture of inert gases.

14.7 Colloidal State

While investigating the diffusion of various substances, Thomas Graham in 1861 found that substances like NaCl, urea, sugar, salts and other crystalline substances easily pass through animal and vegetable membranes, whereas substances like starch, glue, gelatin, silicic acid and proteins do not pass through these membranes. On the basis of the ability of substances to pass through a vegetable or animal membrane, he classified substances into two categories. Substances that could easily pass through animal and vegetable membranes were termed as **crystalloids**, whereas those that could not pass through animal and vegetable membranes were termed as **colloids** (in Greek, *kolla* means glue). However, later it was found that every substance irrespective of its nature can be a crystalloid or a colloid depending upon the environmental conditions. For example, NaCl is a crystalloid in water but behaves like a colloid in benzene. Similarly, soap is a colloid in water but acts as a crystalloid in alcohol. Further studies on the behavior of these solutes showed that the nature of a substance whether colloid or crystalloid depends upon the particle size. When the size of the particle is between 10^{-9} m (1 nm) to 10^{-7} m (100 nm), it behaves like a colloid and if the particle size is less than 10^{-9} m (1 nm) it behaves like a crystalloid. **Thus, colloid is not a substance but it is a state of a substance that depends upon the molecular size.** Colloidal state may be defined as follows

A substance is said to be in the colloidal state when it is dispersed in another medium in the form of very small particles having diameter between 10^{-9} and 10^{-7} m, that is 1 and 100 nm.

Three types of solution

On the basis of the size of the dispersed particles, solutions may be of three types.

- (i) True solution (ii) Suspensions (iii) Colloidal solutions.
- (i) **True solution** It is a 'homogeneous' solution that contains small solute particles (molecules or ions) dispersed through the solvent. The size of the particles is less than 1 nm and it is invisible even under an ultramicroscope. The particles can easily pass through animal or vegetable membrane. For example, solution of sodium chloride in water.
- (ii) **Suspension** It is a 'heterogeneous' mixture containing suspended insoluble particles. The size of the particles is greater than 100 nm. The particles in a suspension may be visible to naked eye or may be seen easily under a microscope. They cannot pass through animal or vegetable membrane or through an ordinary filter paper. For example, dirt particles in water.
- (iii) **Colloidal solution** It is a heterogeneous solution containing particles of intermediate size (diameter between 1 and 100 nm). Such particles are normally not visible to the naked eye but can be seen easily under an ultramicroscope. The particles of a colloidal solution can pass through an ordinary filter paper but not through animal or vegetable membrane. For example, milk, starch solution, etc.

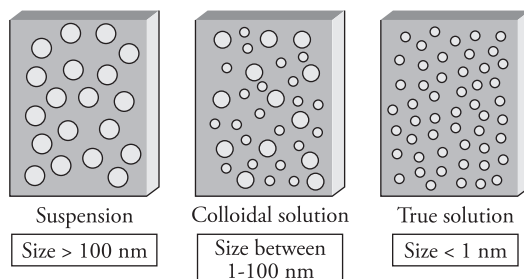


Figure 14.7 *Three types solutions*

Table 14.3 Various characteristic properties of a true solution, colloidal solution and suspension

	Property	Suspension	Colloidal solution	True solution
1	Nature	Heterogeneous	Heterogeneous	Homogeneous
2	Particle size	Greater than 100 nm or (1000 Å or 10^{-5} cm)	Between 1 and 100 nm or (10 Å–1000 Å or 10^{-7} – 10^{-5} cm)	Less than 1 nm or 10 Å or 10^{-7} cm
3	Visibility	The particles are visible under a microscope or even to the naked eye	Particles can be viewed only under an ultramicroscope or an electron microscope, but are invisible even under very powerful microscope	The particles are invisible under all conditions
4	Diffusion of particles	Do not diffuse	Diffuse very slowly	Diffuse rapidly
5	Filtration	They can be filtered even through an ordinary filter paper	They can pass through an ordinary filter paper but not through animal or vegetable membrane, hence they can be filtered with animal or vegetable membranes	They cannot be filtered
6	Settling of particles	Settle under gravity	Settle only on centrifugation	Do not settle
7	Appearance	Opaque	May be opaque, translucent or have a slight color	Transparent
8	Molecular weight of dispersed phase	Low	High	Low
9	Osmotic pressure $O.P \propto 1/\text{mol wt}$	High	Low	High
10	Electrophoresis	Do not exhibit	Exhibit	Do not exhibit
11	Brownian movement	Do not exhibit	Exhibit	Do not exhibit
12	Tyndall effect	Do not exhibit	Exhibit	Do not exhibit
13	Diffusion of particles	Do not diffuse	Diffuses slowly	Diffuse rapidly
14	Coagulation	They are not coagulated	They can be coagulated by adding suitable electrolytes	They can be precipitated by adding suitable electrolytes

Note: The terms ultrafiltration, Tyndall effect, Brownian movement and electrophoresis have been discussed in the properties of colloids (Section 14.11).

Phases of colloidal solutions

A colloidal solution is a heterogeneous system. It consists of two essential components

- (i) **Dispersed phase** It is the component present in smaller proportion just like a solute in a solvent. The dispersed phase is sometimes referred to as the *inner phase* or the *discontinuous phase*.
- (ii) **Dispersion medium** It is the medium in which the dispersed phase is present. It is analogous to the solvent in a solution. This phase is also referred to as the *outer phase* or the *continuous phase*.

Besides the above-mentioned phases, a colloidal solution may also contain a stabilising agent, which is a substance that tends to keep the colloidal particles apart avoiding their coalescence and consequent settling. Some colloids are self-stabilisers.

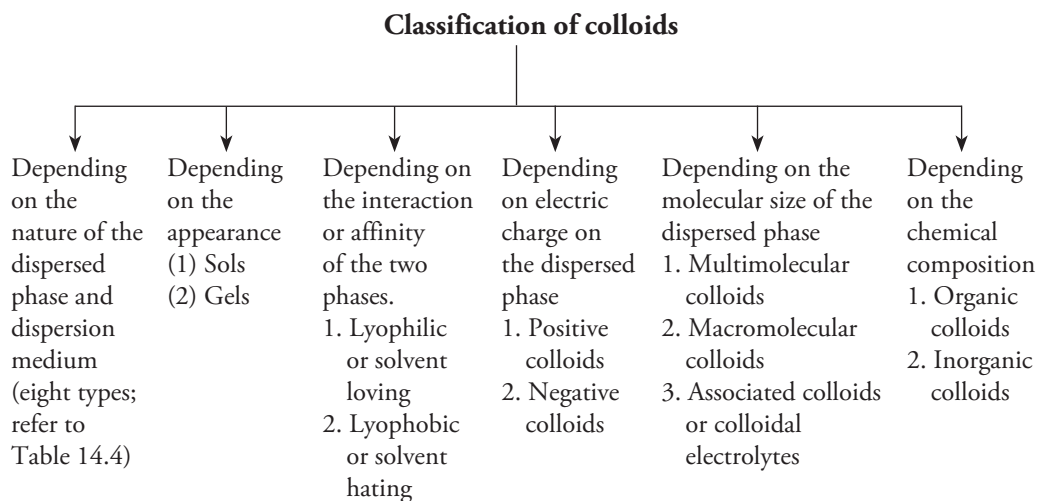
Dispersed phase + dispersion medium = dispersion system (colloidal solution).

On the basis of the nature of the dispersion medium, some specific names have been assigned to the colloidal solutions

Dispersion medium	Water	Alcohol	Benzene	Air
Name of colloidal solution	Hydrosols	Alcosols	Benzosols	Aerosols

The term **sol** is applied to the dispersion of a solid in a liquid, solid or gaseous medium. **Emulsion** is a system in which a liquid is dispersed in another liquid and if a colloidal system becomes fairly rigid it is termed as a **gel**. When gaseous particles are dispersed in a liquid or solid the colloidal system is termed as a **foam**.

14.8 Classification of Colloids



1. **Depending on the nature of the dispersed phase and that of the dispersion medium** On this basis, colloidal solution can be of eight types.

Table 14.4 Type of colloids on the basis of nature of dispersed phase and that of the dispersion medium

Dispersed phase	Dispersion medium	Name of colloidal solution	Examples
Gas	Liquid	Foam	Soap lather, whipped cream, soda water, froth on beer, lemonade froth
Gas	Solid	Solid foam	Pumice stone, foam rubber, cake, bread
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide spray
Liquid	Liquid	Emulsion	Milk, cream, butter, medicines, emulsified oils
Liquid	Solid	Gel	Curd, pudding, cheese, jellies, boot polish
Solid	Gas	Aerosol	Smoke, dust storm, haze
Solid	Liquid	Sol	Paints, inks, starch dispersed in water, gold sol, protein, arsenic sulphide sol
Solid	Solid	Solid sol	Alloys, colored glass (glass with dispersed metals or metal salts), gem stones, ruby glass

2. **Depending upon the appearance** On the basis of appearance, the colloids are divided into two categories:
- Sol** When a colloidal solution appears as a fluid it is referred to as *sol*. Sols are named after the dispersion medium. For example, when the dispersion medium is water, the sol is known as hydrosol or aquasol, if benzene is the dispersion medium then benzosol, if alcohol is the dispersion medium then alcosol and so on.
 - Gel** When a colloidal solution has a solid-like appearance it is referred to as *gel*. They are rigid and rigidity varies from substance to substance. Some common gels are curd, jelly, cheese, etc.
3. **Depending upon the affinity of the two phases** Depending on the attraction between the dispersed phase and dispersion medium, the colloidal solution may be
- Lyophilic colloids or solvent loving** Lyophilic colloids are those colloids in which the particles of the dispersed phase and dispersion medium have affinity (or love) for each other. These are also referred to as *intrinsic colloids*. When water is the dispersion medium they are termed as hydrophilic colloids or emulsoids. These solutions are easily formed, they are self-stabilised and are not easily precipitated by the addition of electrolytes. Lyophilic colloids are reversible in nature. Common examples are glue, gelatin, starch, proteins, rubber and most organic colloids.
 - Lyophobic colloids or solvent hating** Lyophobic colloids are those colloids in which there is no affinity or attraction between the dispersed phase and the dispersion medium. They are also called *extrinsic colloids*. As the dispersed phase and the dispersion medium do not have affinity for each other, these substances have the tendency to change into a

suspension and are brought into colloidal state with great difficulty. These are irreversible in nature and are stabilised by adding small amount of electrolyte. When water is the dispersion medium they are termed as hydrophobic colloids or suspensions. Common examples are the solution of metals like Ag and Au, hydroxides like $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$, metal sulphides like As_2S_3 , etc.

For comparison of lyophilic and lyophobic colloids, refer to Table 14.5.

4. **Depending upon electric charge on the dispersed phase** On the basis of the nature of charge on the dispersed phase there are two types of colloidal solutions
 - (i) **Positive colloids** When the dispersed phase in the colloidal solution carries a positive charge it is termed as a positive colloid. Examples include metal hydroxides like $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$ in water. Other examples are TiO_2 , methylene blue sols, etc.
 - (ii) **Negative colloids** When the dispersed phase in the colloidal solution carries a negative charge, it is termed as a negative colloid. Examples include As_2S_3 sol in water, which carries a negative charge. Other common examples are copper and gold sol, certain dye stuffs like eosin, congo red, etc.
5. **Depending on the molecular size of the dispersed phase** On the basis of molecular size of the dispersed phase, colloids are of three types
 - (i) **Multimolecular colloids** These are colloidal solutions in which the colloidal particles form aggregates of atoms or small molecules each having diameter less than 1 nm. The atoms or molecules in these aggregates are held together by weak van der Waals forces of attraction. These colloids are lyophobic in nature. Examples are gold sol in water consists of dispersed particles of various sizes containing several atoms. Similarly, a sulphur sol consists of a dispersed phase containing large number of particles containing eight sulphur atoms (S_8).
 - (ii) **Macromolecular colloids** In these colloidal solutions, the dispersed particles are large molecules/macromolecules of colloidal dimensions. They can be natural polymers like starch, cellulose and proteins or synthetic polymers like polythene, polystyrene, nylon and plastics. These are lyophilic sols.
 - (iii) **Associated colloids or colloidal electrolytes** At low concentration, the colloidal particles in this type of colloidal solutions behave as normal electrolytes, but at higher concentration they form aggregated particles of colloidal dimensions. These are also referred to as micelles. For example, in dilute solution sodium stearate behaves as an electrolyte but at higher concentration it behaves as a colloid. Other examples are soaps, synthetic detergents, etc.
6. **Depending on the chemical composition** On the basis of their chemical composition they can be
 - (i) **Organic colloids** They are organic in nature. Examples include starch, proteins, rubbers, etc.
 - (ii) **Inorganic colloids** They are inorganic in nature. Examples include sols of Ag, Au, As_2S_3 , etc.

Table 14.5 Lyophilic and lyophobic colloids

S.No	Lyophilic colloids	Lyophobic colloids
1	Also called intrinsic sols	Also termed as extrinsic sols
2	The dispersed phase and the dispersion medium have affinity or love for each other	The dispersed phase and the dispersion medium do not have affinity or attraction for each other
3	They can be prepared easily by merely shaking or warming with the dispersion medium. They are self-stabilised	They are very difficult to prepare. Special methods are used for their preparation. Addition of stabilisers is a must for their stability
4	Small quantity of electrolytes have no effect but large quantities cause coagulation	Coagulation occurs on the addition of even small quantities of electrolyte
5	They are reversible. Once precipitated they pass into colloidal state by contact with the dispersion medium	They are irreversible. Once precipitated they do not pass again easily into colloidal state
6	Surface tension of lyophilic colloids is lower than that of the dispersion medium	Surface tension of the lyophobic colloids and the dispersion medium are almost similar
7	Viscosity is much higher than that of the medium	Viscosity is almost the same as that of the medium
8	These particles cannot be detected readily even under an ultramicroscope because they show faint Tyndall effect	These particles can be easily detected by an ultramicroscope because they show distinct Tyndall effect
9	They can easily set to jelly	They do not gelatinise rapidly
10	They are very stable and are coagulated with difficulty	They are less stable and are coagulated easily
11	They have relatively high osmotic pressure, depression in freezing point and high lowering of vapor pressure	They have high osmotic pressure, small depression in freezing point and less lowering of vapor pressure
12	Particles are heavily solvated	Particles are poorly solvated
13	Example Albumin, glycogen, rubber, starch, ink, etc.	Examples Colloidal gold, colloidal silver, colloidal As_2S_3 , etc.

14.9 Preparation of Colloids

Preparation of lyophilic colloids In lyophilic colloids, the dispersed phase has a strong affinity for the dispersion medium. Therefore, these colloids can be prepared easily by simply mixing the dispersed phase and the dispersion medium under ordinary conditions. For example, gum readily dissolves in water at room temperature. Colloidal solutions like gelatin and starch can be prepared by heating them with water.

Preparation of lyophobic colloids Lyophobic colloids can be prepared by two methods: (i) condensation methods and (ii) dispersion methods.

1. **Condensation methods** In condensation methods, particles of colloidal dimensions are obtained by condensing small particles of the dispersed phase. The following physical and chemical methods can be used.

I Physical methods

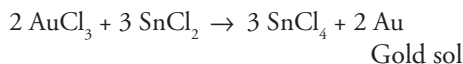
- (a) **Solvent exchange** Colloidal solutions of some substances can be prepared by dissolving it in a solvent in which it is soluble and then pouring it in a solvent in which it is either less soluble or insoluble. For example, colloidal solution of sulphur and phosphorus can be prepared by first dissolving them in alcohol and then pouring the alcoholic solution in excess of water. Alcohol is then removed by dialysis. Such colloidal solutions are however unstable.
- (b) **Excessive cooling** A colloidal solution of ice is obtained by freezing a mixture of water and organic solvent such as chloroform, pentane or ether.
- (c) **Condensation of hot vapor under a liquid phase** Sols of certain elements can be prepared by condensing their vapors in the cooled dispersion medium. For example, sols of mercury and sulphur are prepared by passing their vapors through cold water containing a suitable stabiliser such as ammonium salt or citrate.
- (d) **Controlled condensation** Colloidal sols of certain insoluble substances are prepared by precipitating them in the presence of some protective colloids like starch, gelatin, gum or agar-agar. For example, a sol of Prussian blue is obtained by precipitating it in the presence of starch.

II Chemical methods

- (a) **Oxidation** This method is used to make sols of some non-metals. For example, if H_2S gas is passed through a solution of bromine water or sulphurdioxide, a colloidal sol of sulphur is obtained.



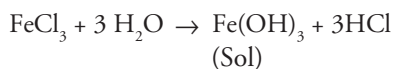
- (b) **Reduction** The colloidal solutions of metals are obtained by reduction of their compounds. For example, a solution of AuCl_3 is reduced with SnCl_2 .



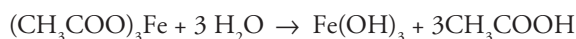
The gold sol thus prepared has a purple color and is called *purple of cassius*.

Similarly, silver sol can be obtained by the reduction of AgNO_3 solution containing alkaline dextrin as stabiliser with different reducing agents.

- (c) **Hydrolysis** Colloidal solution of many oxides and hydroxides can be prepared by this method. For example, if a concentrated solution of ferric chloride is added drop by drop to hot water, a colloidal solution of ferric hydroxide is obtained.

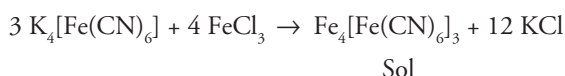


A beautiful red sol of ferric hydroxide can also be prepared by boiling ferric acetate in a beaker having distilled water.

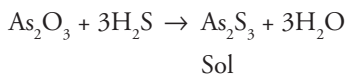


To stabilise the sol thus obtained, excessive CH_3COOH is removed immediately by electrodialysis.

- (d) **Double decomposition** This method is generally employed for preparing the sols of insoluble salts. For example, very dilute solutions of FeCl_3 and $\text{K}_4[\text{Fe}(\text{CN})_6]$ are mixed to prepare a colloidal sol of Prussian blue.



Similarly, by passing H_2S through dilute solution of arsenious oxide in water As_2S_3 sol is obtained.



2. **Dispersion or disintegration methods** Disintegration means to break. Therefore, in this method large lumps are broken down into smaller particles of colloidal dimensions. Various methods employed are as follows

- (a) **Mechanical dispersion** This method is useful for the preparation of colloidal solutions of rubber, inks, paints and varnishes. In this method, the substance is powdered, and on shaking the powdered substance with the dispersion medium a coarse suspension is obtained. This suspension is introduced into a colloidal mill. The mill consists of two steel discs nearly touching each other and rotating in opposite directions with high speed (about 7000 revolutions per minute) (Fig. 14.8). The size of the colloidal particles can be controlled by adjusting the space between the discs. The colloidal sols are then stabilised by adding suitable protective colloid like gum arabic.

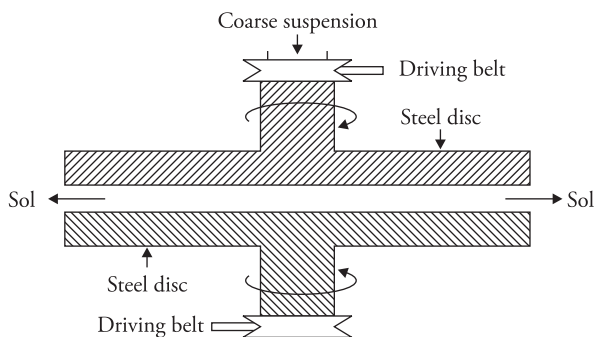


Figure 14.8 Colloidal mill

- (b) **Electric dispersion or Bredig's arc method** It is used for preparing sols of metals such as gold, silver, copper, lead, platinum, etc. An arc is struck between two metal electrodes (made of metal whose sol is to be prepared) held close together and immersed in the dispersion medium like water (Fig. 14.9). The dispersion medium is kept cold by immersing the container in a bath containing freezing mixture. The intense local heat of the arc vaporises the metal rods to form vapor of the metal that is condensed immediately in the dispersion medium to give particles of colloidal dimensions. Small amount of alkali (KOH) stabilises the colloidal solution thus formed.

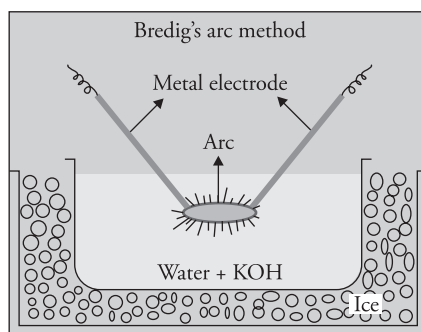


Figure 14.9 Bredig's arc method

- (c) **Peptisation** In this method, freshly precipitated ionic solids are converted into colloidal form by the addition of small quantities of a suitable electrolyte. The electrolyte used for this purpose is called peptising agent or dispersing agent. The peptising agent must have a common ion with the precipitate or solid to be dispersed. For example,
- (i) Freshly precipitated $\text{Fe}(\text{OH})_3$ can be peptised by adding small amount of FeCl_3 solution. A reddish brown colloidal solution is obtained. During peptisation, the suitable ions from the added electrolyte are adsorbed by the particles of the precipitate. The charged particles repel one another to form a colloidal solution. In the above example, Fe^{3+} ions from ferric chloride are adsorbed by $\text{Fe}(\text{OH})_3$ precipitate.

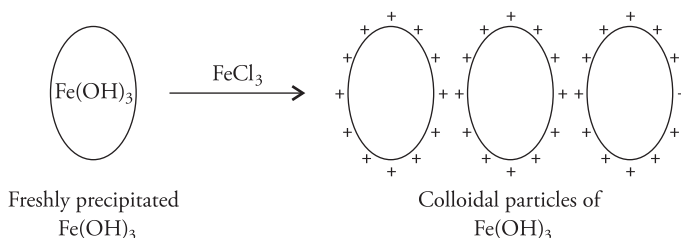
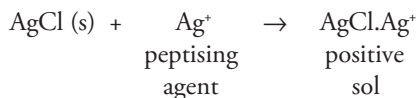


Figure 14.10 Peptisation

- (ii) Freshly precipitated silver chloride can be peptised by shaking it with a dilute solution of silver nitrate to give a colloidal solution of silver chloride.



14.10 Purification of Colloidal Solutions

In the preparation methods described above, the resulting sol contains besides colloidal particles appreciable amount of electrolytes. These impurities destabilise the colloidal sols and hence must be eliminated. The purification of the colloidal solutions can be carried out by the following methods

- (i) **Dialysis** Dialysis is used to separate colloidal particles from soluble impurities (crystalloids and electrolytes). Animal membranes or parchment paper is used for this purpose. They have very fine pores. These pores permit ions of electrolytes to pass through them but they do not allow the colloidal particles to pass through.

An apparatus called the dialyser is used for this purpose. It consists of a bag made of cellophane or parchment. The bag is filled with colloidal solution and is placed in running water in a trough. The soluble impurities gradually diffuse out leaving behind the pure colloidal solution. However, dialysis is a slow process and it takes several hours and sometimes even days for complete purification.

Electrodialysis In this process, dialysis is carried out under the influence of electric field. This speeds up the migration of ions to the oppositely charged electrodes.

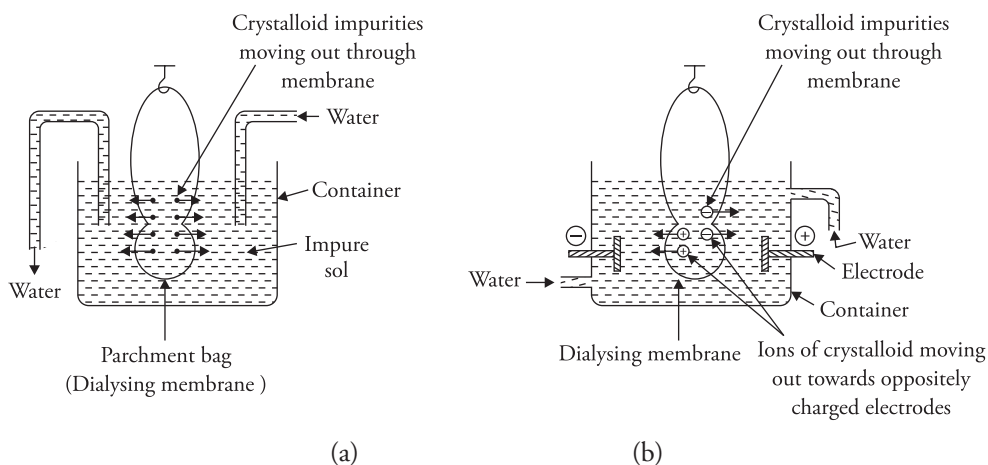


Figure 14.11 (a) A dialysis cell and (b) electrodialyser

- (i) **Ultrafiltration** The process of separating the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called ultrafiltration. The pores of ordinary filter paper are large (1030 nm) and the colloidal particles can easily pass through them.

When this filter paper is impregnated with collodion or gelatin and hardened by dipping in a solution of HCHO and finally drying, the size of the pores is reduced. The ions and molecules of impurities pass through these pores but colloidal particles are retained.

Ultrafiltration finds use in the separation of bacteria from their solution.

14.11 Properties of Colloidal Solutions

The main characteristic properties of colloidal solution are as follows.

1. **Heterogeneous nature** Colloidal solutions are heterogeneous solutions. They consist of two distinct phases (i) dispersed phase and (ii) dispersion medium. Because of the small size of their particles, they appear homogeneous to the naked eye but their heterogeneity is confirmed by seeing under electron microscope and by experiments like dialysis, ultrafiltration and ultracentrifugation.
2. **Filterability** As the size of the pores of an ordinary filter paper is bigger than the size of colloidal particles, these particles can easily pass through the ordinary filter paper. However, animal membrane, vegetable membrane and ultrafilters do not permit the colloidal particles to pass through them.
3. **Stability** The colloidal particles are quite stable and do not settle at the bottom of the container.
4. **Colligative properties** Compared with true solutions, the colloidal solutions have lesser number of particles per liter because of their high molecular weights. As the colligative properties depend upon the number of the particles, these sols boil and freeze at almost the same temperature as the pure dispersion medium. The lowering of the vapor pressure is also negligible. Of all the properties the osmotic pressure alone has measurable value and its measurement has been used for finding the average particle weight in colloidal solutions.
5. **Mechanical properties**
 - (a) **Brownian movement** It was observed by an English botanist, Robert Brown, in 1927, that in aqueous suspensions the pollen grains were in a constant zig-zag motion. When the colloidal solutions were observed under an ultramicroscope, a similar zig-zag motion was seen in them. This was termed as the 'Brownian movement' after the name of the discoverer.

Wiener (1863) stated that the cause of these movements is the constant collisions between the particles of the dispersed phase and the molecules of the dispersion medium. Wiener said that the impact of the dispersion medium particles is unequal. When a molecule of dispersion medium collides with a colloidal particle, it is displaced in one direction until its direction and speed of motion is altered by another collision. This process gives rise to a zig-zag motion (Fig. 14.12). However, as the size of the dispersed particles increases the chances of unequal collision decreases. That is why a suspension does not show any such movement because of their large molecular size.

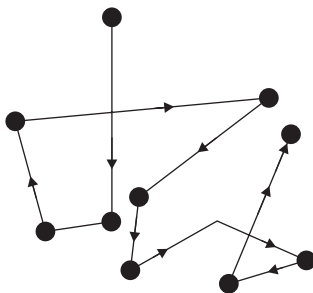


Figure 14.12 *Brownian movement, zig-zag movement of colloidal particles*

- (b) **Diffusion** As the size of the colloidal particles is big, they diffuse slowly from higher concentration to low concentration region.
 - (c) **Sedimentation** Colloidal solutions are quite stable and remain suspended indefinitely. However, colloidal particles of large size settle very slowly under gravity. This phenomenon called sedimentation is used to determine the molecular masses of these particles.
6. **Optical properties: Tyndall effect**

If a true solution is placed in a dark room and a strong beam of light is passed through it, then the path of light is not visible. However, when a strong beam of light is passed through a sol placed in a dark room and viewed at right angles, the path of light becomes visible. The path of light appears as a hazy beam or a cone. This effect was studied by Tyndall in 1869 and is popularly known after his name as the Tyndall effect. The illuminated path or beam of light is termed as the Tyndall beam or the Tyndall cone.

The Tyndall effect is believed to occur because of the scattering of light by the colloidal particles. The sol particles absorb the incident light and then scatter it in all directions. The path of light becomes visible in the direction at right angles to the direction of the incident light as maximum light is scattered at right angles to the direction of the incident light. As the particles in true solution are too small, they do not cause scattering; hence, Tyndall effect is not observed in true solutions.

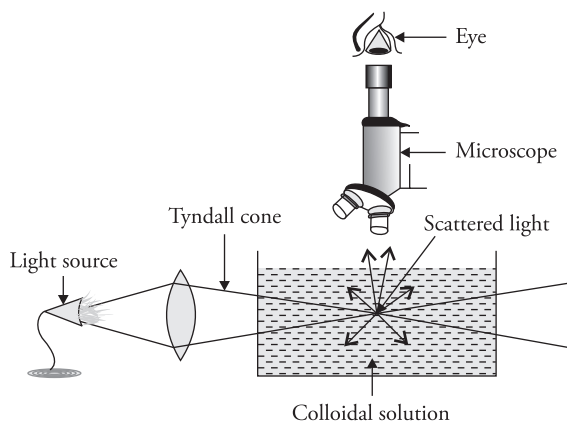


Figure 14.13 *Tyndall effect*

7. **Electrical properties** The colloidal particles have electric charge. They have been classified on the basis of their charge as positive and negative colloids (refer to the classification of colloids Section 14.8). Electrophoresis helps to ascertain the presence of charge on the sol particles. It also helps to determine the nature of charge (whether positive or negative).

- (i) **Electrophoresis (or cataphoresis)** The movement of colloidal particles on the application of an electric field is called electrophoresis or cataphoresis.

If the colloidal particles are positively charged, they will be discharged near the negative electrode. On the other hand, if the colloidal particles are negatively charged they will be discharged at the positive electrode.

To study the phenomenon of electrophoresis, a U-tube having platinum electrodes in each limb is taken. As_2S_3 sol is taken in the U-tube. Before electrophoresis, the color intensity in both the limbs is the same. On passing electric current through this sol, the color of the sol near the positive electrode becomes intense. An increase in color intensity at the positive electrode clearly shows that under the influence of electric field the As_2S_3 sol has migrated to that electrode. Hence, it shows that the As_2S_3 sol bears a negative charge.

Similarly, accumulation of $\text{Fe}(\text{OH})_3$ sol near the negative electrode under the influence of electric current shows that it bears a positive charge.

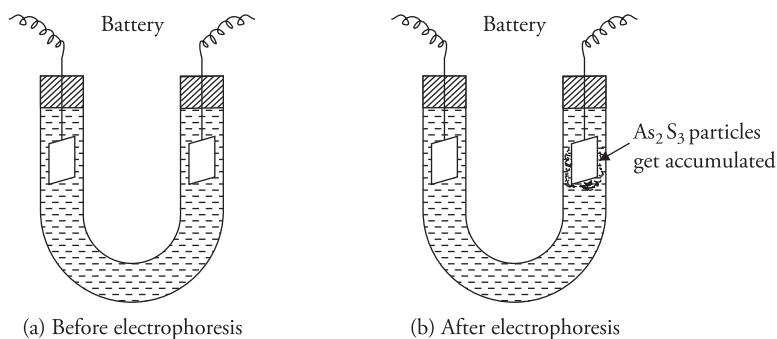
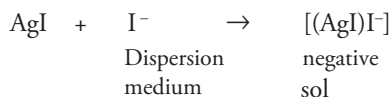


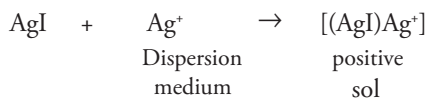
Figure 14.14 Electrophoresis

Origin of charge The origin of charge on the colloidal particles have been explained by many theories but the most accepted view is the *preferential adsorption of ions*. According to this view, the colloidal particles adsorb positive or negative ions on their surface preferentially and hence acquire a positive or negative charge. It may be noted here that the preferential adsorption of those ions occurs, which are common with the ions of the dispersion medium. For example, silver iodide sol can be prepared in two ways.

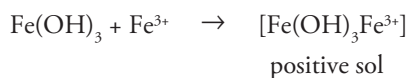
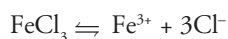
- *By adding silver nitrate to an aqueous solution of potassium iodide:* In this case, iodide ions of the dispersion medium are common with the AgI formed, hence they are adsorbed preferentially and the sol acquires a negative charge.



- *By adding potassium iodide to an aqueous solution of silver nitrate:* In this case, silver ions of the dispersion medium are common with the AgI formed; hence they are adsorbed preferentially and the sol acquires a positive charge.



Similarly, hydrolysis of FeCl_3 gives a positively charged $\text{Fe}(\text{OH})_3$ sol because Fe^{3+} ions are adsorbed preferentially.



Some common examples of positive and negative colloids are given in the Table 14.6.

Table 14.6 Common examples of positive and negative colloids

Positively charged sols	Negatively charged sols
Hydroxides like $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$, $\text{Ca}(\text{OH})_2$	Sulphides like As_2S_3 , CdS , Sb_2S_3 , etc.
Oxides like TiO_2	Metallic sols like Cu, Ag, Au, Pt, etc.
Basic dyes like methylene blue	Acidic dyes like eosin, congo red, etc.
Haemoglobin, proteins in acid solution	Organic sols like gelatin, starch, etc.

- (ii) **Electro-osmosis** If in electrophoresis a partition is made between the two electrodes using a parchment paper or animal membrane so that the colloidal particles do not pass through it but there is movement of dispersion medium under the influence of electric field. *This movement of the dispersion medium relative to the dispersed phase under the influence of the electric field when the two electrodes are separated by a semipermeable membrane is known as electro-osmosis.* This is indicated by the rise of water level in one limb of the U-tube.
- (iii) **Isoelectric point** Lyophilic colloids like albumin, gelatin, starch, etc., are positively charged in acid because of the adsorption of H^+ ions and negatively charged in the presence of alkali because of the adsorption of OH^- ions on the surface. This shows that there must be some intermediate H^+ ion concentration at which the particles are neither positive nor negative. This is the isoelectric point at which the colloidal particles move neither to the anode nor to the cathode under the influence of an electric field. Thus, the isoelectric point in case of colloids may be defined as '*the concentration at which the colloidal particles have no charge is known as the isoelectric point*'.

Coagulation of colloidal solutions

As discussed in the earlier sections, the colloidal particles are charged particles. They can either be positively charged or can bear a negative charge. Like charges repel each other and prevent the colloidal particles from coming close to each other. Hence, the colloidal solution is stabilised. If this charge is neutralised by the addition of an oppositely charged electrolyte, then the colloidal particles come closer to each other and form large aggregates and precipitate out. This phenomenon of precipitation of colloidal particles is termed as *coagulation or flocculation*. The precipitate formed after coagulation is known as the **coagulum**. Coagulation can be brought about in the following ways

- **By electrophoresis** This method is used for the coagulation of lyophobic colloids. Under the influence of electric field, the colloidal particles are discharged at the oppositely charged electrode. On reaching the electrode they get discharged and coagulate.
- **Mutual coagulation** Coagulation can be brought about by mixing oppositely charged sol. For example, coagulation of positively charged $\text{Fe}(\text{OH})_3$ sol can be affected by mixing it with negatively charged As_2S_3 in proper proportions. The charges on both the sols are neutralised and both get coagulated.
- **By addition of electrolytes** The colloidal particles can be coagulated by the addition of excess of oppositely charged electrolytes. These oppositely charged electrolytes neutralise the charge on the colloidal particles and bring about their coagulation. For example, negatively charged As_2O_3 sol can be readily coagulated by the addition of BaCl_2 solution. The Ba^{2+} ions neutralise the negative charge of As_2O_3 sol and coagulate it. Similarly, the OH^- ions of NaOH neutralise the positive charge of $\text{Fe}(\text{OH})_3$ sol and coagulate it.

The coagulating effect of electrolytes on hydrophobic sols was studied by Schulze, Hardy, Linder and Picton. They said that the electrolytes have different coagulation capacities. A colloidal particle is precipitated by an ion carrying charge opposite to that of the colloidal particle. Such an ion is called the **active ion or flocculating ion**. The coagulation capacity of this ion depends upon its valency. According to the **Hardy–Schulze rule**, *greater the valency of the active ion or the flocculating ion, greater will be its coagulating power*. Thus, the coagulating power of different cations to precipitate a negative sol As_2S_3 decreases in the order



Similarly for precipitating $\text{Fe}(\text{OH})_3$, a positive sol, the coagulating power of different anions decreases in the order



The coagulating power of an electrolyte or ion is determined experimentally by finding the minimum concentration in millimoles per liter required to bring about coagulation or flocculation of a sol. This is termed as its **flocculation value** and is expressed in millimoles per liter. The flocculating value for the coagulation of positively charged $\text{Fe}(\text{OH})_3$ sol and negatively charged As_2S_3 sol are given in Table (14.7).

Table 14.7 Flocculating values in millimole/liter of common electrolytes

Ferric hydroxide (+) sol			Arsenic sulphide (–) sol		
Electrolyte	Active ion (anion)	Flocculating value (millimoles/liter)	Electrolyte	Active ion (cation)	Flocculating value (millimoles/liter)
KCl	Cl [–]	103	NaCl	Na ⁺	51
KBr	Br [–]	138	KCl	K ⁺	50
K ₂ SO ₄	SO ₄ ^{2–}	0.210	MgSO ₄	Mg ²⁺	0.72
Na ₂ C ₂ O ₄	C ₂ O ₄ ^{2–}	0.238	BaCl ₂	Ba ²⁺	0.69
K ₃ [Fe(CN) ₆]	[Fe(CN) ₆] ^{3–}	0.096	AlCl ₃	Al ³⁺	0.093

14.12 Stability of Colloids

Following factors contribute to the stability of the colloidal solutions

1. *Electric charge* A colloidal sol is stable when the colloidal particles have similar type of charge in them. Particles with like charges repel each other and mutual repulsion prevents them from coming closer to each other and forming aggregates resulting in coagulation.
2. *Solvation* It is the tendency to bind with the solvent. The solvent molecules surround the colloidal particles and thus stop them from coming closer to each other and coagulating. This can be illustrated by considering the example of proteins at the isoelectric point, where the protein particles are uncharged. Although under these conditions the stability of protein particles is minimum, they do not precipitate because they are enveloped by a layer of water. If, however, this layer is removed then coagulation occurs.
3. *Stabilising by protecting films* Certain protective agents can be added to colloidal systems to enhance their stability. The protective agent gets adsorbed on the surface of the dispersed particles, coating them and thus preventing them from coming in contact with each other.

14.13 Protective Colloids

Addition of small amount of electrolytes brings about the precipitation of lyophobic sols such as those of metals like gold and silver. When a lyophilic colloid like gelatin, gum arabic, agar-agar, etc, is added to this lyophobic colloid its stability is greatly enhanced. Now this lyophobic colloid does not coagulate by the addition of small amount of electrolytes. This action of lyophilic colloids to prevent precipitation is termed as protection and the lyophilic colloid added for protection is termed as the *protective colloid*. For example, gelatin acts as a protective colloid and when it is added to a gold sol, the latter is not easily precipitated on adding sodium chloride. Similarly, addition of gelatin to As₂S₃ makes the latter stable towards the electrolytes.

Gold number It is used to express the protecting power of different protective colloids. This term was introduced by Zsigmondy. It is defined as ‘*The number of milligrams of protective colloid required to just prevent precipitation of 10 mL of a given sol when 1 mL of a 10% solution of sodium chloride is added to it.*’ Smaller the gold number of a protective colloid, higher is its protective power. Gold numbers of some protective colloids are given in Table 14.8.

Table 14.8 Gold number of some protective colloids

Protective colloid	Gold number
Gelatin	0.005–0.01
Starch	15–25
Gum arabic	0.15–0.25
Egg albumin	0.1–0.2
Haemoglobin	0.03–0.07

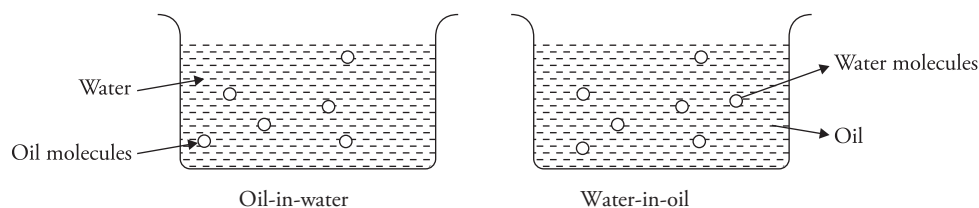
The above list shows that gelatin is the best protective colloid. The protective action of a lyophilic colloid is because of the formation of a protective layer around the lyophobic colloid (due to adsorption). The electrolyte particles cannot penetrate this protective layer easily, hence they are unable to neutralise the charge on colloidal particles and bring about coagulation.

14.14 Emulsion

An emulsion is a colloidal solution in which two or more immiscible liquids are dispersed in one another in the form of finely divided liquid droplets. The most common examples of emulsions are milk (soluble fat dispersed in water), butter (water dispersed in liquid fat), etc. Emulsions are generally obtained by mixing oil with water. As the two phases in an emulsion are immiscible, emulsions are generally unstable and a suitable stabilising agent called an emulsifier or emulsifying agent is added. Commonly used emulsifiers are gum, soap, glass powder, etc.

Type of emulsions These are of two types: (i) oil-in-water type and (ii) water-in-oil type.

- (i) **Oil in water (O/W) type** When the dispersed phase (small amount) is oil and the dispersion medium (excess) is water it is termed as oil-in-water type emulsion. Examples of such type of emulsions are milk (soluble fats in water), vanishing cream, etc. These emulsions are also called **aqueous emulsions**.
- (ii) **Water-in-oil (W/O) type** When the dispersed phase is water and the dispersion medium is oil, then the emulsion is termed as water-in-oil type emulsion. Examples include butter, cold cream, etc. These emulsions are also called **oily emulsions**.

**Figure 14.15** Types of emulsion

It may be noted that the two types of emulsions can be interconverted by simply changing the ratio of the dispersed phase and the dispersion medium.

Identification of emulsions

The following tests can be used to differentiate the two types of emulsions.

- (i) **Dilution test** Add water to the emulsion. If the emulsion is diluted on addition of water it is an oil-in-water type emulsion. In case it is not diluted, then it is a water-in-oil type emulsion where oil is present in excess and is the dispersion medium.
- (ii) **Dye test** Add an oil-soluble dye to the emulsion and shake the mixture. If the color spreads throughout the whole emulsion then oil is the dispersion medium and if the color of the dye appears as droplets then the emulsion is oil-in-water type and oil is the dispersed phase.

Stability of emulsion Emulsions are generally unstable and are stabilised by the addition of a third component known as the emulsifier. Emulsifier decreases the surface tension of the two liquids and reduces the chances of tiny drops to coalesce and form aggregates. Soaps, detergents, gums, proteins, agar-agar, etc., are the commonly used emulsifying agents. An emulsifier acts in two ways.

- (i) It may be more soluble in one liquid than the other; in such a case, it forms a protective film around the liquid in which it is less soluble and prevents the drops from coming together coalescing, consequently separating into two layers.
- (ii) The emulsifier may be soluble in both the liquids but is not equally wetted by the two. For example, soot particles or lamp black particles are wetted more by kerosene oil than water; hence, they remain more in contact with kerosene and hence stabilise the emulsion of water in kerosene oil.

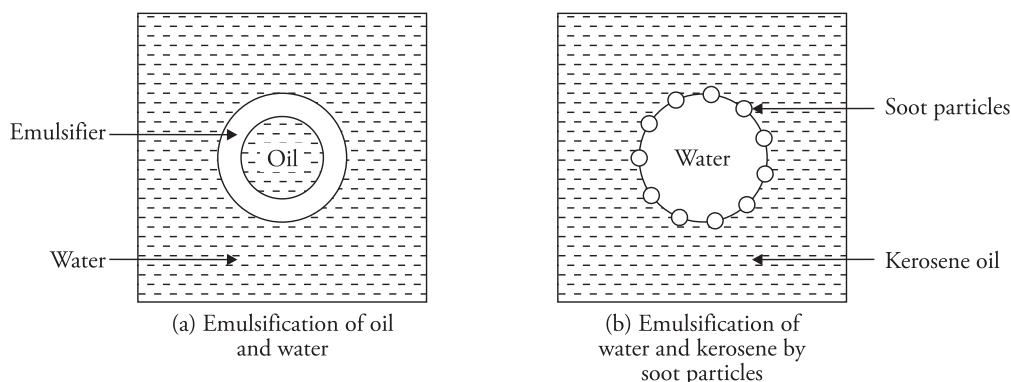


Figure 14.16 (a) Emulsification of oil and water; (b) emulsification of water and kerosene by soot particles

Demulsification The process of decomposing the emulsion back into its constituent liquids is called demulsification. It can be brought about by centrifugation, filtration, freezing one component, distilling off one component, extracting one component by solvent extraction, heating under high pressure and other chemical methods.

Applications of emulsions Emulsions find manifold uses in various fields.

- (i) *Medicines* Many medicines are in the form of emulsions. Common examples are cod liver oil, castor oil, etc.
- (ii) *Articles in daily use* Milk and ice cream are emulsions. Other examples include hair cream, cold cream, vanishing creams, different lotions, paints, varnishes and liquid polishes.
- (iii) *In industry* Latex obtained from rubber tree is an emulsion of negatively charged rubber particles in water. The froth floatation process employed in the concentration of sulphide ore. In this process, oil emulsions are added to finely divided ore and the foam produced by bubbling air contains the ore.

Emulsions of oil and fats are used in leather industry for softening leather. In agriculture, various liquids in the form of emulsions are sprayed on the crops.

Gels

A gel is a jelly-like colloidal system in which a liquid is dispersed in a solid medium. Common examples of gel are curd, jellies, fruit jam and cheese. Other examples are silicic acid gel in water, sodium oleate gel in water, etc. The process of gel formation is called gelation. When a lyophilic colloid is coagulated the dispersion medium (liquid) gets trapped inside the colloid, resulting in the formation of a semisolid jelly-like porous mass called a gel.

Uses

- Silica gel is used as a dehydrating agent.
- Gelatin, agar-agar gel are utilised in laboratories.
- Curds and jellies are edible gels.
- Boot polishes also have a gel-like structure.

14.15 Micelles

At low concentrations, certain substances behave as normal electrolytes and form true solutions but at higher concentrations they aggregate to form particles of colloidal dimensions. These are called micelles. For example, molecules of soaps and detergents are smaller than the colloidal size, hence they behave as normal strong electrolytes at low concentration. However, in concentrated solutions these substances form aggregates or clusters and exhibit colloidal properties. Such aggregate particles are called *micelles*. Thus, micelles are clusters or aggregate particles formed by the association of particles in concentrated solution. Soaps and detergents are the common examples of micelles. As stated earlier micelle formation occurs in concentrated solution. ***The concentration above which micelle formation starts is termed as the critical micellization concentration (CMC).*** Different micelles have different CMC value. The CMC value of sodium stearate ($C_{17}H_{35}COONa$) is $10^{-3} \text{ mol L}^{-1}$. When the concentration is less than this value they behave as a normal electrolyte and if the concentration is higher, they aggregate together and behave as micelles. Change from ions to micelles is reversible. Other examples of micelles are.

Sodium palmitate ($C_{15}H_{31}COONa$)

Sodium lauryl sulphate $CH_3(CH_2)_{11}SO_3O^-Na^+$

14.16 Applications of Colloids

Colloids have important applications in nature and in day to day life. Some of them are

1. *Medicines* Colloidal medicines being finely subdivided can be easily adsorbed by the body. Colloidal gold and calcium are used as tonics. Colloidal sulphur is used as a germ killer. Cod liver oil used as a tonic is an emulsion. Milk of magnesia used to cure acidity is also an emulsion.
2. *Everyday life* Colloids form an important part of our diet and articles of daily usage. Blood, protoplasm, curd, milk, butter and cheese are all colloidal in nature. Besides this various creams, lotions, boot polishes are also colloidal in nature.
3. *In Industry*
 - (a) *Water purification* Electrolytes like alum are used to precipitate the colloidal impurities present in water. The positive charge on Al^{3+} ions neutralises the negatively charged colloidal impurities in water. Consequently, the impurities coagulate and settle down.
 - (b) *Tanning of leather* Skins and hides are positively charged colloidal sols of proteins. They are coagulated by adding negatively charged sol of tannin present in the tree bark. As a result, the surface of leather becomes hard.
 - (c) *In laundry* The colloidal soap solution removes the dirt and grease particles by adsorption or emulsification of the greasy matter. The emulsion is easily washed with water.
 - (d) *Rubber industry* Latex from rubber tree is a negative sol of rubber particles. Rubber is obtained from latex by coagulation using a suitable electrolyte.
 - (e) *Sewage disposal* The charged colloidal particles of the sewage are coagulated by passing sewage water through plates kept at high potential (electrophoresis). The colloidal particles are discharged at oppositely charged electrodes and get coagulated.
 - (f) *Smoke precipitation (Cottrell's precipitator)* Carbon particles in air are colloidal and negatively charged. Smoke particles are passed through a chamber having metal plates maintained at high potential. The carbon particles are removed by the principle of electrophoresis.
 - (g) *Photography* Sensitive emulsions are deposited on photographic plates. The films are fine suspensions of silver bromide in gelatin.
 - (h) *Artificial rain* The clouds contain charged colloidal particles. When oppositely charged dust or sand particles are sprayed over the clouds the charge of the colloidal particles is neutralised. They coalesce into bigger drops causing artificial rain.
 - (i) *In Nature*
 - (a) *Formation of Delta* Charged colloidal particles are present in river water. When these particles come in contact with sea water containing electrolytes (salts), they coagulate and settle at the point of contact leading to delta formation.
 - (b) *Blood* It is a negative colloid; hence, bleeding can be stopped by adding alum that contains Al^{3+} ions.
 - (ii) *Analytical applications* Colloids find use in gravimetric analysis, qualitative analysis and identification of traces of noble metals and can also be used in the distinction of natural honey from artificial honey.

Summary

- The phenomenon of attracting and retaining molecules on the surface is termed as adsorption.
- Absorption is the process in which the molecules enter in the bulky material.
- Sorption is the process where the molecule is first adsorbed and then it enters in the bulk.
- When the adsorbed molecules are held by van der Waals forces, it is called physical adsorption and if the molecules form bond with the surface it is termed as chemisorption.
- Variation of adsorption with pressure is explained by adsorption isotherm. They are of two types Freundlich adsorption isotherm and Langmuir adsorption isotherm.
- Size of colloidal particles range from 1 to 100 nm and they cannot pass through animal or vegetable membrane.
- The zig-zag movement of colloidal particles is termed as Brownian motion.
- Colloidal solution of two immiscible liquids is called emulsion. It can be oil-in-water type or water-in-oil type.
- At low concentrations, certain substances behave as normal electrolytes and form true solutions but at higher concentrations they aggregate to form particles of colloidal dimensions. These are called micelles.

Review Questions

1. Define the terms adsorption, adsorbate and adsorbent.
2. What is adsorption? Highlight the major differentiating points between adsorption and absorption.
3. What are physical and chemical adsorptions? Differentiate between the two.
4. Define adsorption. Discuss the various factors which affect the adsorption of a gas on solid adsorbent.
5. Derive the Freundlich adsorption isotherm. What are its limitations?
6. On what assumption did Langmuir derive his adsorption isotherm? Derive it and explain how it justifies the experimental results of adsorption at different pressure.
7. What are colloids? Differentiate between a suspension, true solution and a colloidal solution.
8. Define colloids and classify them in detail.
9. Write short notes on
 - (i) Lyophilic and lyophobic colloids.
 - (ii) Protective colloids.

- (iii) Dialysis
 - (iv) Ultrafiltration
 - (v) Origin of charge on colloidal particles
 - (vi) Emulsions
 - (vii) Micelles
 - (viii) Tyndall effect
 - (ix) Brownian movement
 - (x) Hardy–Schulze law
 - (xi) Electrical properties of colloids
10. What are colloids? Write in detail the various methods employed for their preparation.
 11. Explain the following
 - (i) Emulsions
 - (ii) Gold number
 - (iii) Critical micellisation concentration
 - (iv) Gels
 - (v) Stability of emulsions
 12. Write in detail the applications of colloids in various fields.

Multiple Choice Questions

1. The difference between crystalloid and colloid is of

(a) Solubility	(b) Diffusion
(c) Particle size	(d) Chemical composition
2. Which of the following forms a colloidal solution in water

(a) Glucose	(b) Starch
(c) Sodium chloride	(d) Barium nitrate
3. Which of the following is not a colloidal solution of gas in solid

(a) Pumice stone	(b) Foam rubber
(c) Bread	(d) Mist
4. The size of colloidal particle ranges from

(a) 1 to 10 Å	(b) 10 to 100 Å
(c) 20 to 50 Å	(d) 1 to 280 Å
5. Arsenious sulphide sol and ferric hydroxide sol are

(a) Positive and negative colloids respectively
(b) Negative and positive colloids respectively
(c) Both are positive colloids
(d) Both are negative colloids

6. Which of the following sols is hydrophobic
 - (a) Sulphur
 - (b) Starch
 - (c) Gum
 - (d) Gelatin
7. Which is incorrect in case of lyophobic sol
 - (a) Dispersed particles are weakly hydrated
 - (b) Dispersed phase is generally inorganic in nature
 - (c) They are reversible in nature
 - (d) They can be easily coagulated.
8. Which of the following is an example of solid – solid colloidal solution
 - (a) Pumice stone
 - (b) Cake
 - (c) Synthetic gems
 - (d) Butter
9. Metals like silver and copper can be obtained in the colloidal state by
 - (a) Bredigs arc method
 - (b) Dialysis
 - (c) Peptisation
 - (d) Coagulation
10. Ions preferentially adsorbed by arsenious sulphide and silver chloride are
 - (a) Sulphide and silver ions respectively
 - (b) Arsenious and silver ions respectively
 - (c) Sulphide and chloride ions respectively
 - (d) Arsenious and chloride ions respectively
11. Micelle is a term used for the aggregates formed in solution by
 - (a) Colloidal non – electrolytes
 - (b) Colloidal electrolytes
 - (c) Non associated colloids
 - (d) All the above
12. The presence of charge on colloidal particles can be shown by
 - (a) Dialysis
 - (b) Brownian movement
 - (c) Electrophoresis
 - (d) Tyndall effect
13. Tyndall effect in a colloidal solution is due to
 - (a) Absorption of light
 - (b) Presence of charged particles
 - (c) Scattering of light by colloidal particles
 - (d) Reflection of light by colloidal particles.
14. Hardy – Schulz law states that
 - (a) Greater the valency of the active ion greater is the power to cause coagulation
 - (b) Charge of cation and anion has no effect on the coagulation power of colloids
 - (c) Sols are coagulated only by those ions whose charge is similar to that of the sol.
 - (d) Non electrolytes increase the coagulation power of colloids.
15. Which of the following has maximum coagulating power in the coagulation of positively charged sol
 - (a) Cl^-
 - (b) SO_4^{2-}
 - (c) PO_4^{3-}
 - (d) $[\text{Fe}(\text{CN})_6]^{4-}$

16. At isoelectric point
 - (a) Colloidal particles become stable
 - (b) Colloidal particles carry no charge
 - (c) Peptisation occurs
 - (d) Coagulation is not possible.
17. Gold number indicates
 - (a) Protective action of lyophilic colloid.
 - (b) Protective action of lyophobic colloid.
 - (c) Amount of gold dissolved in a given sol.
 - (d) Charge on gold sol.
18. Gold number is minimum in case of

(a) Egg albumen	(b) Gelatin
(c) Gum Arabic	(d) Starch
19. Emulsifier is a substance which

(a) Coagulates the emulsion	(b) Stabilises the emulsion
(c) Homogenises the emulsion	(d) Accelerates dispersion of liquid in liquid
20. When the dispersion medium is gas, the colloidal system is known as

(a) Aerosol	(b) Alcosol
(c) Benzosol	(d) Hydrosol
21. Cloud burst occurs because
 - (a) Large amount of water is present in the cloud
 - (b) Clouds are attracted by electric charge of the earth
 - (c) The oppositely charged particles get mutually discharged resulting in the coagulation of water droplets
 - (d) Dense clouds are present in the upper atmosphere
22. The change in concentration in the interfacial layer between two phases of a system by surface forces is called

(a) Adsorption	(b) Absorption
(c) Sorption	(d) Occlusion
23. According to Langmuir adsorption isotherm which one of the following is correct

(a) $\frac{x}{m} = \alpha$	(b) $\frac{x}{m} \propto p$
(c) $\frac{x}{m} = \frac{1}{p}$	(d) $\frac{x}{m} > p$

24. Which of the following expression holds good for the Freundlich adsorption isotherm

(a) $\frac{x}{m} = kp^{\frac{1}{n}}$

(b) $\frac{x}{m} = p^{\frac{1}{n}}$

(c) $\frac{x}{m} = p^2$

(d) $\frac{x}{m} = \left(\frac{k}{p}\right)^{\frac{1}{n}}$

25. Adsorption plays an important role in

(a) Heterogeneous catalysis

(b) Homogeneous catalysis

(c) Positive catalysis

(d) Negative catalysis

Solutions

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (c) | 2 (b) | 3 (d) | 4 (b) | 5 (b) | 6 (a) | 7 (c) | 8 (c) |
| 9 (a) | 10 (a) | 11 (b) | 12 (c) | 13 (c) | 14 (a) | 15 (d) | 16 (b) |
| 17 (a) | 18 (b) | 19 (b) | 20 (a) | 21 (c) | 22 (a) | 23 (b) | 24 (a) |
| 25 (a) | | | | | | | |

Chapter 15

THERMODYNAMICS

15.1 Introduction

In our day-to-day life, we come across several instances in which one form of energy is converted into another form. When you rub your hands they become hot; similarly, if a piece of metal is hammered, it becomes hot. In both the above examples, mechanical energy is converted into heat energy. On the other hand, you are well aware that when water is heated, steam is generated, which is used to move turbines for the generation of electricity. Here, heat energy produces mechanical work. There can be numerous examples for the conversion of one form of energy into another. *The science that deals with the interconversion of heat to work or any other form of energy is termed as thermodynamics.* The term is self-indicative of what is happening – “thermo” is from temperature, which means energy and ‘dynamics’ pertains to motion or work. Chemical thermodynamics is a portion of thermodynamics that deals with the study of the processes in which chemical energy is involved.

The principles of interconversion of energy in various forms are summarized in the three basic laws of thermodynamics. The first law is a statement of the law of conservation of energy, that is, energy cannot be created or destroyed, it can merely be converted from one form to another. The second law of thermodynamics explains the occurrence of various reactions spontaneously. It introduces the concept of ‘entropy’ or ‘disorder’ or ‘randomness’ to predict the spontaneous occurrence of chemical reactions. The third law of thermodynamics relates, among other things, to the experimental approach to absolute zero.

Thermodynamics is a powerful tool for chemists. It studies the relationship between the effects of temperature on physical systems at the macroscopic scale. It helps in predicting whether a reaction will occur or not. It also helps to predict the direction in which a chemical reaction will occur.

However, thermodynamics does not show how fast a reaction will proceed. Let us now deal with the fundamental concept of thermodynamics.

15.2 Terminology of Thermodynamics

It is necessary to define certain terms and expressions commonly used in thermodynamics.

(I) System and surroundings

System A thermodynamic system may be defined as that portion of the universe which is under observation or study.

Surroundings It is the portion of the universe that is not a part of the system.

The real or imaginary surface separating the system from the surroundings is called the boundary. The system and surroundings can interact across the boundary.

Let us illustrate these terms taking a simple example. Suppose we place alcohol and water in a beaker and we wish to study the behavior of alcohol in water. Then the constituents of the beaker (alcohol and water) constitute the system, the beaker is the boundary and everything outside the beaker constitutes the surroundings.

1. Types of walls or boundaries

- (i) **A rigid wall** It is a wall whose shape and position are fixed.
- (ii) **An impermeable wall** It is a wall that does not permit the passage of matter.
- (iii) **Adiabatic wall** A wall that allows neither matter nor energy to pass through it is an adiabatic wall, for example, a thermos bottle; universe is a perfect example of an adiabatic system.
- (iv) **Diathermal wall** A wall that does not allow the matter to pass through it but allows the passage of energy is termed as a diathermal wall. For example, the walls of a metal container are diathermal.

2. Types of systems

- (i) **Isolated system** An isolated system exchanges neither matter nor energy with its surroundings. A hot liquid kept in a thermos flask is an example of an isolated system because it can neither gain or lose energy nor it can gain or lose matter.
- (ii) **Closed system** A closed system can exchange energy but not matter with its surroundings. A hot liquid in a stainless steel flask is an example of a closed system because gradually heat is lost and the liquid cools but there is no exchange of matter.
- (iii) **Open system** An open system can exchange both matter and energy with its surroundings. For example, a hot liquid kept in an open container as it can lose both energy and matter. It cools because of loss of energy and loses matter in the form of vapors.
- (iv) **Homogeneous system** If the physical and chemical properties are similar throughout the system then it is a homogeneous system, that is, it is completely uniform and does not contain any boundary surfaces separating different parts of the system.

For example, a mixture of gases, a solution of salt or sugar in water or a mixture of two miscible liquids are all examples of homogeneous systems because it is not possible to distinguish between the different gases or between salt and water or between the two liquids.

- (v) **Heterogeneous system** A heterogeneous system has two or more phases that are separated from each other by distinct boundaries. Different portions of a heterogeneous system have different physical and chemical properties. For example, ice and water, mixture of two immiscible liquids (benzene and water), sand and water.

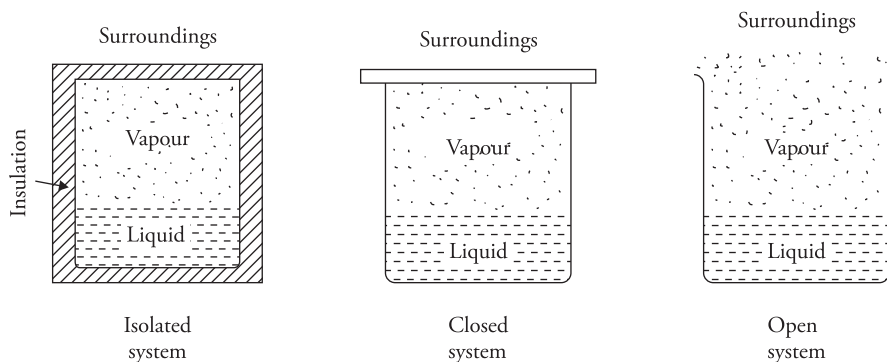


Figure 15.1 Different types of systems

3. Macroscopic properties of the system

The properties of the system that arise from the bulk behavior of matter are called macroscopic properties. The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

The macroscopic properties (observable properties) can be divided into two types:

(i) intensive properties and (ii) extensive properties.

- (i) **Intensive properties** Intensive properties are those whose value does not depend on the quantity of substance present in the system. Such properties do not require any specification of the size of sample to which they refer. For example, temperature is an intensive property because if we take 400 mL of water in a beaker kept at room temperature and divide it into four parts containing 150, 100, 80 and 70 mL or in any other proportion, the temperature of each part of water will be the same.
- (ii) **Extensive properties** Those properties whose value depends upon the quantity of substance present in the system are called extensive properties. Its value is additive. Suppose a system X is divided into subsystems a_1, a_2, a_3 ; let Y be the property of the system A and y_1, y_2, y_3 are the properties of the respective subsystems a_1, a_2, a_3 , then Y is an extensive property if $Y = y_1 + y_2 + y_3$. For example, mass is an extensive property.

The extensive and intensive properties are listed in Table 15.1.

Table 15.1 Various extensive and intensive properties

Extensive property	Intensive property
Mass	Temperature
Volume	Pressure
Surface area	Viscosity
Energy	Surface tension
Enthalpy	Dielectric constant
Entropy	Specific heat capacity
Free energy	Vapor pressure

Heat capacity	Refractive index
	Boiling point, freezing point
	Molar enthalpy
	Molar entropy
	Chemical potential
	Free energy per mole.

4. State of a system and state variables

When the macroscopic properties of a system such as pressure, volume and temperature have a fixed value, then the system is said to be in a particular state. If the macroscopic properties of the system change, then the state of the system is said to have changed. Hence, the state of a system is defined by its macroscopic properties.

State variables

The fundamental properties such as pressure, volume, temperature and composition that describe the state of a system are known as the state variables or state properties or thermodynamic parameters.

It is not essential to specify all the variables for describing the state of a system. For example, in a homogeneous system consisting of a single substance composition is automatically fixed and the system can be defined by three variables: pressure, volume and temperature, which are inter-related by the gas equation $PV = RT$, where R is the gas constant. If P and T are specified, then V automatically becomes fixed and can be found by the gas equation. Hence, only two variables are required to specify or describe the state of the system.

5. Thermodynamic functions (variables) or state function

There are some thermodynamic variables that depend on the manner in which the system reaches a particular state like the work performed at constant pressure is different from the work performed at constant volume; hence, work done is a path-dependent function. On the other hand, there are some variables that do not depend on the path of the reaction and depend only on the initial and final states of the system. Such variables whose value depends only on the initial and final states of the system and not on the manner or path in which the system reaches that state are called *thermodynamic functions or state functions*. Conventionally, these functions are denoted by capital letters. Examples of the state function are temperature (T), pressure (P), volume (V), internal energy (E or U), enthalpy (H), entropy (S) and free energy (G or F).

6. Thermodynamic equilibrium

If the intensive properties of a system do not change with time, then the system is said to be in a state of thermodynamic equilibrium. At equilibrium, energy or matter does not flow within the system or at its boundaries. Thermodynamic equilibrium requires that the following three types of equilibrium exist simultaneously in the system:

- (i) **Thermal equilibrium** If the temperature is same throughout the whole system then the system is said to be in thermal equilibrium.
- (ii) **Chemical equilibrium** If a system consists of more than one substance, then the system will be in chemical equilibrium if the composition of the system does not change

with time. The chemical equilibrium is a dynamic process in which the rates of forward and backward reactions become equal.

- (iii) **Mechanical equilibrium** A system is said to be in a state of mechanical equilibrium if there is no flow of matter within the system or at its boundaries.

7. Thermodynamic processes

When a system changes from one state to another, then the path or the process by which such a change occurs is called the thermodynamic process. The following processes generally occur:

- (i) **Isobaric process** When the change occurs at constant pressure, then the process is said to be isobaric. For example, if water at 25 °C converts into vapor at 100 °C in an open vessel, then both the processes occur at the same pressure, that is, atmospheric pressure, hence, it is an isobaric process. Isobaric processes are always accompanied by change in volume.
- (ii) **Isochoric process** In an isochoric process, the volume remains constant, that is, $dV = 0$. For example, combustion in a bomb calorimeter is an isochoric process.
- (iii) **Isothermal process** When the temperature remains constant during the process, it is called an isothermal process. In this process, a system may exchange heat with the surroundings to maintain the constancy of temperature.
- (iv) **Adiabatic process** In an adiabatic process, the system neither gives nor takes heat from the surroundings. However, the temperature of the system may change. Examples of adiabatic process are as follows:

(i) Sudden bursting of a cycle tube, (ii) compression of a mixture of oil vapor and air during compression stroke of an internal combustion engine.

In an adiabatic process, the temperature falls if the process is endothermic, for example, bursting of tube; rises if the process is exothermic, for example, compression of IC engine.

- (v) **Cyclic process** When a system undergoes a number of changes and then returns to its original state, then the process is a cyclic process and the path of the process is called a cycle.
- (vi) **Reversible process** A reversible process is one in which the direction of the process may be reversed at any stage by merely a small change in a variable like temperature, pressure, etc. Therefore, in a reversible process the force driving the operation is only infinitesimally greater than the opposing force and the process is carried out infinitesimally slowly. In such a process, the system and the surroundings are almost always in equilibrium with each other.
- (vii) **Irreversible process** An irreversible process is one in which the state properties of a system differ from those of its surroundings by a finite amount, and hence the system does not remain in equilibrium with its surroundings. The driving force is very different from the opposing force. All natural processes are irreversible processes.

8. Energy

In mechanics, energy is defined as the capacity to do work. Mechanical energy is classified into two fundamental types

- (i) **Potential energy** Potential energy is the energy stored because of its position.
- (ii) **Kinetic energy** Kinetic energy is the energy because of the motion.

In any system, the total energy is the sum of potential and kinetic energies. Similarly, the energy associated with molecules can be broadly divided into two categories

- (a) **External energy** It is the sum of the kinetic and potential energies of the system. It is of little importance in chemical changes and hence is ignored.
- (b) **Internal or intrinsic energy** Internal energy is one of the most important quantities in thermodynamics. Every substance has energy associated with the rotational, vibrational and translational movement of its molecules. All types of energies associated with the internal processes like attraction between electrons and protons, mutual repulsion between electrons, etc, constitute the internal energy or intrinsic energy. It is denoted by E (or sometimes U).

It is not possible to find out the absolute value of internal energy of a system. For thermodynamic studies, the change in internal energy has a greater significance. Internal energy depends only on the initial and final states of the system and not on the path followed; hence, it is a state function. Moreover, it is an extensive property as its value depends upon the amount of substance.

15.3 Zeroth Law of Thermodynamics

This law was formulated after the first and second laws of thermodynamics. This law is based on the concept of thermal equilibrium.

Let us consider three systems A, B and C placed together. A and C are at different temperatures. When they come in contact with each other, they attain thermal equilibrium and acquire the same temperature. B and C that are also at different temperatures initially attain thermal equilibrium when placed in contact with each other. According to the zeroth law of thermodynamics, if there is thermal equilibrium between A and C and also between B and C, then A and B will also be in thermal equilibrium, that is, A, B and C will be at the same temperature.

If $A(T_A) \rightleftharpoons C(T_C)$ and $B(T_B) \rightleftharpoons C(T_C)$,

then $A(T_A) \rightleftharpoons B(T_B)$

and $A(T_A) \rightleftharpoons B(T_B) \rightleftharpoons C(T_C)$.

15.4 First Law of Thermodynamics

The first law of thermodynamics is merely a statement of the principle of conservation of energy. It states that energy can neither be created nor destroyed; it can only be transformed from one form to another. This law has been universally accepted as till date there has been no exception to this law.

Different statements of the first law of thermodynamics

The first law can be stated in several ways, all of which are equivalent to each other. Some selected statements are as follows:

1. First statement

As a result of experiments performed by Joule, he stated that 'The amount of work done and heat generated are exactly equivalent'. In Maxwell's words, Joule's statement can be restated

as 'When heat and work are interconverted, the amount of work done is equivalent to the amount of heat supplied'.

2. **Second statement**

'Although energy may be transformed from one form to another, the energy of an isolated system must remain constant,'

3. **Third statement**

'Energy in one form, if it disappears, will make its appearance in an exactly equivalent quantity in another form'.

4. **Fourth statement**

'It is not possible to design a perpetual motion machine that could produce work without spending an equivalent amount of energy on it'.

Mathematical formulation of the first law

Before formulating the first law, let us make ourselves familiar with the symbols and sign conventions that will be used for heat, work and the internal energy.

- (i) **Heat** It is represented by ' q '. When the system absorbs heat from the surrounding, it is denoted by $+q$ and when the system releases heat to the surroundings it is denoted by $-q$.
- (ii) **Work** It is represented by the symbol ' w '. According to the latest SI convention work done on the system is positive and work done by the system is negative. Hence work of contraction is positive work and the work of expansion is negative work.
- (iii) **Internal energy change** Change in internal energy is represented by ΔE or ΔU (the present text will use the symbol ΔE). The increase in internal energy of the system is denoted by $+\Delta E$ and the decrease in internal energy of the system is represented by $-\Delta E$.

Suppose, the heat supplied to a gaseous system in equilibrium is q , a part of this heat will be used up by the system in doing work against the surroundings during the expansion of the gaseous system and the rest of the heat will increase the internal energy of the system. Thus, from the first law, we get

Heat supplied to the system = increase in internal energy + work done by the system

$$q = \Delta E - w$$

$$\text{or } \Delta E = q + w \quad (1)$$

This equation is a mathematical expression of the first law.

In Eq. (1), it may be noted that

- (i) As E is a state function, the change in internal energy ΔE does not depend on the path of the system. It depends on the initial and final states of the system.
- (ii) q and w are not state functions. They depend on the path of the process. As they do not represent state properties, conventionally they are denoted by small letters.

In order to understand this point more clearly, let us consider a system in state A. It changes to state B by path I and returns to state A by a different path IV (Fig. 15.2).

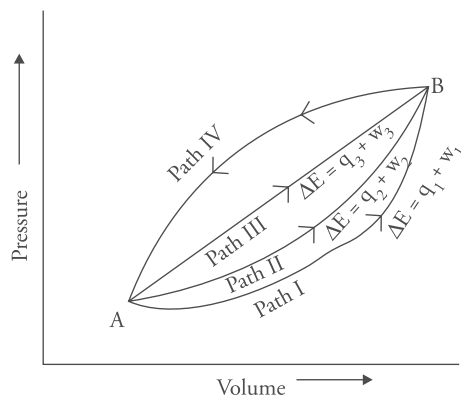


Figure 15.2 Energy as a function of state ($\Delta E = E_B - E_A$)

If the internal energy input by path I is less than the internal energy output by path IV, then there would be a net gain of internal energy when the cycle is complete. Hence, by repeating the process continuously the system would be gaining internal energy from nowhere. This is impossible and is contrary to the first law of thermodynamics. From the first law, the total internal energy in the forward process and the return process should be equal. Thus, internal energy is independent of the path and depends only on the initial and final states of the system. This shows that E is a state function. For a cyclic process, that is, a system returning to its initial state after passing through a series of changes, the change in internal energy ΔE is zero. Mathematically, it can be represented as

$$\oint dE = 0 \text{ (cyclic integral of } dE \text{ is zero).}$$

Hence, it is clear that internal energy is a state function. Let us suppose that there are three different paths by which a system in state A can go to state B (Fig. 15.2). In all these cases, the change in internal energy $\Delta E = E_B - E_A$ will be the same whether it goes by path I or path II or path III. If the heat involved in paths I, II and III is q_1 , q_2 and q_3 , respectively, and the work involved in the three paths is w_1 , w_2 and w_3 , respectively, then

$$\Delta E = q_1 + w_1$$

$$\Delta E = q_2 + w_2$$

$$\Delta E = q_3 + w_3$$

The values q_1 , q_2 and q_3 as well as w_1 , w_2 and w_3 are different for different paths. Hence, q and w are not state functions but their difference is always constant.

Differential form of the first law

For an infinitesimal process equation, Eq. (1) takes the form

$$dE = \delta q + \delta w \quad (2)$$

An infinitesimal process may be defined as a process involving only infinitesimal change in the thermodynamic variables of the system. Equation (2) is the differential form of the first law. In the above equation, it is important to note that dE is a perfect or exact differential, whereas δq and δw are inexact differentials. E is a state function and change in internal energy does not depend on the path or previous history of the system. E can be differentiated and dE can be integrated. In fact, the differential of all the state properties, such as P, V, T , etc., are exact differentials. On the other hand, q and w are not state functions and changes in their magnitudes depend on the path of the system. Hence, q and w cannot be differentiated nor dq and dw be integrated, except under special conditions. In mathematical language, δq and δw are inexact differentials.

Equation for exact differential

Let X be an extensive property of a system, which is a single valued function of its several variables x, y, z, \dots then we can write

$$X = f(x, y, z, \dots).$$

These variables may be pressure, volume, temperature, masses of the constituents and the like, that determine the state of the system. As X is a state property, a small change in X , that is, dX , has the properties of an exact differential.

$$dX = \left(\frac{\partial X}{\partial x} \right)_{y,z} dx + \left(\frac{\partial X}{\partial y} \right)_{x,z} dy + \left(\frac{\partial X}{\partial z} \right)_{x,y} dz + \dots \quad (3)$$

The partial differential notation $\left(\frac{\partial X}{\partial x} \right)_{y,z}$ gives the rate of change of X with respect to the variable x when all the other variables put as subscript remain constant. Equation (3) is a general equation for the exact differential and signifies that the total change dX is equal to the rate of change of X with respect to x multiplied with the change in x , plus similar quantities with respect to y, z .

Now, let us consider the example of internal energy E of a given mass. It depends on any two of P, V and T variables. If E depends on V and T only, then

$$E = f(V, T) \\ \text{or } dE = \left(\frac{\partial E}{\partial V} \right)_T dV + \left(\frac{\partial E}{\partial T} \right)_V dT$$

If E is a function of P and T , then

$$E = f(P, T) \\ \text{or } dE = \left(\frac{\partial E}{\partial P} \right)_T dP + \left(\frac{\partial E}{\partial T} \right)_P dT$$

Similarly, if $V = f(P, T)$, then

$$dV = \left(\frac{\partial V}{\partial P} \right)_T dP + \left(\frac{\partial V}{\partial T} \right)_P dT$$

Concept of work

Work is equal to the force multiplied by the displacement (i.e., distance through which the force displaces an object). We generally come across two kinds of work. These are (i) electrical work and (ii) mechanical work.

Electrical work is important in the system where reaction takes place between ions, whereas mechanical work is performed when a system changes its volume in the presence of external pressure. It is important especially in systems that contain gases. This is also known as the pressure–volume work.

Pressure – Volume work

Consider a cylinder containing an ideal gas fitted with a weightless and frictionless piston of cross-sectional area 'A' (Fig. 15.3). Let the gas exert pressure P on the piston. If the piston is balanced by a confining external force 'F' acting on the piston, then

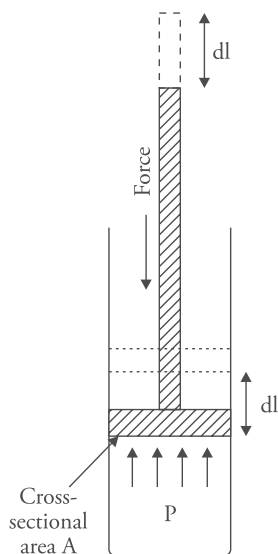


Figure 15.3 *Work of expansion*

$$F = P \times A$$

This shows that at equilibrium the confining pressure, that is, pressure on the gas, is also equal to P .

Now, if the confining pressure is momentarily reduced by a small amount dP , the piston will move out through a small distance dl , and a small amount of work dw will be done by the gas on its surroundings. The work is calculated by multiplying the confining force by the distance through which the force moves, that is,

$$\begin{aligned} \text{Work} &= \text{confining force} \times \text{distance} \\ &= \text{confining pressure} \times \text{area} \times \text{distance} \end{aligned}$$

$$\therefore F = P \times A \quad (1)$$

Thus, work done by the gas is given by

$$\begin{aligned} dw &= -(P - dP) \times A \times dl \\ &= -(P - dP) dV \\ \text{where, } (A \times dl) &= dV, \text{ that is, increase in volume} \end{aligned} \quad (2)$$

$$\begin{aligned} dw &= -PdV + dPdV \\ \text{neglecting the term } dP \times dV, \text{ which is negligibly small, we get} \\ dw &= -PdV \end{aligned} \quad (3)$$

If the volume of the gas is changed from V_1 to V_2 maintaining the values of confining pressure as $(P-dP)$ throughout, then the total amount of work w can be evaluated by integrating Eq. (3) between the limits V_1 and V_2 .

$$w = - \int_{V_1}^{V_2} PdV \quad (4)$$

Thus, substituting this value of w in the expression of the first law of thermodynamics, we have

$$\Delta E = q + \int_{V_1}^{V_2} PdV \quad (5)$$

The Eqs. (4) and (5) are very useful and help in the evaluation of q , w and ΔE in any expansion or contraction of a system. These equations take different forms under different conditions. Some of such conditions are discussed below.

- (i) **Isochoric or constant volume process** When a change is brought about at constant volume, then $dV = 0$ and Eqs (4) and (5) take the form

$$w = 0 \text{ and } \Delta E = q_v \quad (6)$$

Thus, the work done at constant volume is zero and the increase in internal energy becomes equal to the heat absorbed at constant volume q_v .

- (ii) **When the confining pressure is zero** In this case, $P = 0$ and thus the gas is expanding against a vacuum. The work done will be

$$w = -PdV$$

$$\therefore P = 0, \text{ therefore } w = 0$$

Hence, the work done will be zero. This type of expansion is known as free expansion. In this case again,

$$\Delta E = q_p$$

- (iii) **When the confining pressure is constant** If P is constant then the equation $w = -\int_{V_1}^{V_2} P dV$ can be written as

$$w = -P \int_{V_1}^{V_2} dV = -P(V_2 - V_1)$$

$$\text{or, } w = -P\Delta V$$

Substituting the value of w in Eq. (5), we get $\Delta E = q_p - P\Delta V$; here the subscript p denotes that the heat is absorbed at constant pressure.

- (iv) **When the confining pressure is variable** When P is variable, the value of integration of Eq. (4) can be determined graphically by plotting P vs V and determining the area under the curve. Alternatively, if the dependence of pressure on volume is known for a given situation, then P should be replaced by its equivalent terms of V in Eq. (5) and then integrated in the usual way.

\therefore The work done in different processes is different; hence work is path-dependent.

Maximum work and reversibility

As discussed earlier, the magnitude of work done by the gas depends on the opposing or confining pressure and is independent of its own pressure. Let P_g be the pressure of the gas and P be the confining pressure. If $P = 0$, the work done will be zero. The greater the confining pressure, which the gas overcomes in expanding, the greater is the work done by it. If we go on increasing the value of P , more and more work will be done by the gas. Suppose the confining pressure P becomes equal to P_g , then both the pressures will balance each other and no change in volume will take place. If the confining pressure is further increased, then the direction of the process is reversed and now the work will be done on the gas. From the above discussion, it is clear that the maximum work can be obtained only when the opposing or confining pressure remains less than the pressure of the gas by an infinitesimal amount throughout the process. However, these conditions under which maximum work can be obtained are exactly the conditions specified for the reversibility of the process. *It is therefore concluded that the maximum work can be obtained only when the process is carried out reversibly.*

The equation $w = -\int_{V_1}^{V_2} P dV$ has been derived with an assumption that the confining pressure is

infinitesimally smaller than the pressure of the gas. If this condition is maintained throughout the process, then the work obtained will be maximum work. Denoting the maximum work by w_{\max} , the above equation can be written as

$$w_{\max} = -\int_{V_1}^{V_2} P dV \quad (7)$$

As the pressure does not remain constant but is always changing and maintaining its value infinitesimally less than the pressure of the gas, Eq. (7) cannot be integrated unless the pressure is specified in terms of volume. Suppose the cylinder contains n moles of an ideal gas, then with the help of the gas equation $PV = nRT$, the pressure is given by

$$P = \frac{nRT}{V}$$

Substituting in Eq. (7), we get

$$w_{\max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad (\text{the value of } T \text{ is constant})$$

$$\text{or } w_{\max} = -nRT \ln \left(\frac{V_2}{V_1} \right) = -2.303nRT \log_{10} \left(\frac{V_2}{V_1} \right) \quad (8)$$

For an ideal gas, at constant temperature

$$P_1 V_1 = P_2 V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Hence Eq. (8) can also be written as

$$w_{\max} = -nRT \ln \left(\frac{P_1}{P_2} \right) = -2.303nRT \log_{10} \left(\frac{P_1}{P_2} \right) \quad (9)$$

It should be noted that the maximum work obtained under reversible conditions in a given process will be the minimum work required to reverse the process.

Practice problems

1. In a certain process, 430 J of work is done on a system, which gives off 120 J of heat. What is ΔE for the process?

Solution

Work done on the system = 430 J $w = +430 \text{ J}$

Heat liberated by the system = 120 J $q = -120 \text{ J}$

From the first law of thermodynamics,

$$\Delta E = q + w = -120 + 430 = 310 \text{ J.}$$

2. 2 mole of an ideal gas expands from 5 atm pressure to a pressure of 1 atm under reversible conditions at 300 K. Calculate the work done.

Solution

As the expansion is reversible, the amount of work done will be maximum. The work is given by

$$w_{\max} = -2.303nRT \log_{10} \frac{P_1}{P_2}$$

Here $P_1 = 5 \text{ atm}$

$P_2 = 1 \text{ atm}$

$T = 300 \text{ K}$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$n = 2 \text{ moles}$

$$\begin{aligned}
 \therefore w_{\max} &= -2.303 \times 2 \times 8.314 \times 300 \log_{10} \frac{5}{1} \\
 &= -2.303 \times 2 \times 8.314 \times 300 \times 0.6990 \\
 &= -8030.311 \text{ J} \quad (\text{negative sign shows that work is done by the system})
 \end{aligned}$$

3. 5 moles of an ideal gas is filled in a vessel at 25 °C and 5 atm. If the gas is allowed to expand isothermally, calculate the work done when the gas expands
- Into a vacuum
 - Against a constant opposing pressure of 2 atm
 - Under reversible conditions till the value of final pressure reaches 2 atm.

Solution

- This is a case of free expansion because the opposing pressure is zero, hence, the work done by the gas will also be zero, that is, $w = 0$.
- When the opposing pressure is constant, the work done is given by

$$w = -P(V_2 - V_1).$$

Here, $P = 2$ atm and as the pressure of the gas changes from 5 to 2 atm, the volume also changes from V_1 to V_2 .

From the gas equation $V = \frac{nRT}{P}$

$$V_1 = \frac{5RT}{5} \quad \text{and} \quad V_2 = \frac{5RT}{2}$$

$$\begin{aligned}
 \therefore w &= -P(V_2 - V_1) = 2 \left(\frac{5RT}{2} - \frac{5RT}{5} \right) \\
 &= -2 \times 5RT \left(\frac{1}{2} - \frac{1}{5} \right) \\
 &= -2 \times 5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \times \frac{3}{10} \\
 &= -7432.71 \text{ J}
 \end{aligned}$$

- For reversible expansion, the work is given by

$$\begin{aligned}
 w &= -2.303nRT \log_{10} \frac{P_1}{P_2} \\
 w &= -2.303 \times 5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \log_{10} \frac{5}{2} \\
 &= -2.303 \times 5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \times 0.3979 \\
 &= -11351.785 \text{ J}
 \end{aligned}$$

4. An ideal gas of volume 2 L at 0 °C and 5 atm pressure is expanded (a) isothermally and reversibly until the pressure becomes 1 atm and (b) isothermally and irreversibly against a constant pressure of 1 atm. Calculate w , ΔE , ΔH and q in each case.

Solution

(a) Isothermal reversible process

$$PV = nRT \quad n = \frac{PV}{RT} = \frac{5 \text{ atm} \times 2 \text{ L}}{0.0821 \text{ L atm K}^{-1} \times 273.2 \text{ K}} = 0.4458 \text{ mol}$$

$$\begin{aligned} w_{\text{rev}} &= -2.303nRT \log_{10} \frac{P_1}{P_2} \\ &= -2.303 \times 0.4458 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 273.2 \times \log_{10} \frac{5}{1} \\ &= -1630 \text{ J} \end{aligned}$$

For an ideal gas at constant temperature

$$\Delta E = 0 \quad \text{and} \quad \Delta H = 0$$

$$q = \Delta E - w = 0 - (-1630 \text{ J}) = 1630 \text{ J}$$

(b) Isothermal irreversible process

$$w = -P_{\text{ext}} \Delta V = -1 \text{ atm} (V_2 - V_1) \text{ liters}$$

$$V_1 = 2 \text{ liters}$$

$$\text{At constant temperature, } V_2 = \frac{P_1 V_1}{P_2} = \frac{5 \times 2}{1} = 10 \text{ liters}$$

$$w = -1(10 - 2) = -8 \text{ L atm} = -8 \times 101.26 \text{ J} = -810 \text{ J} \quad (1 \text{ L atm} = 101.26 \text{ J})$$

Temperature remaining constant, for an ideal gas

$$\Delta E = 0 \quad \text{and} \quad \Delta H = 0$$

$$q = \Delta E - w = 0 - (-810 \text{ J}) = 810 \text{ J}$$

Practice problems

- One mole of an ideal monoatomic gas at 27 °C expands adiabatically against a constant external pressure of 1 atm from a volume of 5 dm³ to 15 dm³. Calculate q, w and ΔE.
[Ans q = 0; w = -1013 J; ΔE = -1013 J]
- A 5 L cylinder contains 10 mole of oxygen gas at 27 °C. Because of sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmospheric pressure is 1.0 atm, calculate the work done by the gas.
[Ans -24443.7 J]
- 2 moles of an ideal gas at 2 atm at 27 °C is compressed isothermally to one half of its volume by an external pressure of 4 atm. Calculate q, w and ΔE.
[Ans q = -4984 J; w = +4984 J; ΔE = 0]
- 10 L of a monoatomic gas at 0 °C and 10 atm pressure undergoes isothermal expansion to 1 atm. What is the final volume and what is the work done by the gas, if the process is (a) reversible and (b) irreversible.
[Ans V₂ = 100 liters; w_{rev} = -23313 J; w_{irrev} = -9113 J]
- What will be the volume change if 607.8 J of work is done by a system containing an ideal gas? The surroundings exert constant pressure of 10 atm. (1 L atm = 101.26 J) [Ans 0.6 L]

6. 500 cm³ of a sample of an ideal gas is compressed by an average pressure of 0.5 atm to 250 cm³. During this process, 10 J of heat flows out to the surroundings. Calculate the change in internal energy of the system. [Ans = 2.67 J]

Enthalpy and enthalpy change

As mentioned earlier that in most chemical processes where no electrical process is involved, the only work done is the pressure volume work. If $dV = 0$, that is, the volume is constant, then the work done will be zero. For such a process, the equation

$$\Delta E = q + \int_{V_1}^{V_2} PdV \text{ reduces to}$$

$$\Delta E = q_v$$

Hence, the heat absorbed at constant volume is equal to the increase in internal energy of the system. As E is a state property, ΔE does not depend on the path of the process; hence, q_v will also be independent of the path or mechanism of the process and will depend on the initial and final states of the system. Thus, q_v becomes a state function. It may be noted that q is not a state function but when the process is carried out at constant volume, that is, by an isochoric process, then q_v becomes equal to ΔE and thus it becomes a state function.

However, in our day to day life and also most of the experiments in the laboratory conducted at constant pressure, that is, at atmospheric pressure. Hence, heat absorbed at constant pressure is more significant. It will be seen that the heat absorbed in a reaction occurring at constant pressure is also a state function like the heat absorbed at constant volume. Suppose a system changes from state 1 to state 2 at constant pressure P , the volume will increase by ΔV and the work of expansion will be given by $-P\Delta V$. If the amount of heat absorbed by the system at constant pressure is q_p , then according to the first law of thermodynamics

$$\Delta E = q_p - P\Delta V \quad (\because w = -P\Delta V) \quad (10)$$

where ΔE is the increase in internal energy. If E_1 is the internal energy and V_1 the volume of the system at the initial state, and E_2 and V_2 are the corresponding terms at the final state then

$$\Delta E = E_2 - E_1$$

$$\Delta V = V_2 - V_1$$

Substituting these values in Eq. (10) we get

$$E_2 - E_1 = q_p - P(V_2 - V_1)$$

$$\text{or, } q_p = (E_2 + PV_2) - (E_1 + PV_1) \quad (11)$$

Equation (11) shows that q_p is equal to the difference in two terms, each having the form $(E + PV)$. This quantity $(E + PV)$ is termed as the heat content at constant pressure or enthalpy and is denoted by symbol H . Thus, $H = E + PV$.

As E , P and V are state functions, H is also a state function. Thus, from Eq. (11)

$$q_p = H_2 - H_1 = \Delta H \quad (12)$$

where H_1 and H_2 are the heat contents or enthalpies in the initial and final states, respectively, and ΔH is the increase in enthalpy of the system. Hence, from Eq. (12) it follows that the increase in enthalpy of a system is equal to the heat absorbed at constant pressure. As the value of ΔH depends only on the initial and final states of the system, q_p also depends only on initial and final states, hence q_p is a state function.

It may be noted that Eq. (12) holds good when

- The pressure remains constant and
- The work done in the process is only the pressure–volume work

In processes where electrical work is done like in a galvanic cell, q_p will not be equal to the enthalpy change.

Moreover, as the absolute value of E cannot be determined, the absolute value of H cannot be found out. In thermodynamics, the absolute values are of little significance. We are concerned with the change in enthalpy ΔH which is a measurable quantity.

$$\Delta H = \Delta E + P\Delta V.$$

To sum up,

If a system absorbs q amount of heat then,

$$q \text{ (at constant volume)} = \Delta E$$

$$q \text{ (at constant pressure)} = \Delta H \text{ and}$$

The change in enthalpy of the system at constant pressure is equal to the sum of increase in internal energy and pressure–volume work.

Relationship between ΔH and ΔE

As studied earlier ΔH and ΔE are related as

$$\Delta H = \Delta E + P\Delta V$$

Let us consider a chemical reaction taking place at constant temperature (T) and pressure (P). Let the total volume of the gaseous reactants be V_r and the volume of the gaseous products be V_p , n_r is the number of moles of gaseous reactants and n_p is the number of moles of gaseous products, then according to ideal gas equation

$$PV = nRT$$

$$\text{for reactants} \quad PV_r = n_r RT \text{ (at constant } T \text{ \& } P) \quad (i)$$

$$\text{for products} \quad PV_p = n_p RT \text{ (at constant } T \text{ \& } P) \quad (ii)$$

Subtracting Eq. (i) from (ii), we get

$$P(V_p - V_r) = (n_p - n_r)RT$$

$$P\Delta V = \Delta n_g RT \quad (\text{iii})$$

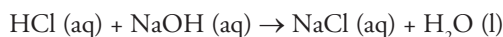
where Δn_g = number of moles of products – number of moles of reactant

Placing the value of $P\Delta V$ from Eq. (iii)

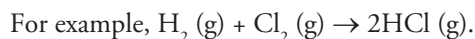
$$\Delta H = \Delta E + \Delta n_g RT$$

It may be noted that ΔH will be equal to ΔE when

- (i) Reactions are carried out in closed vessels of fixed volume, that is, $\Delta V = 0$.
- (ii) Reactions that do not involve gaseous components, for example, reaction between aqueous solution of hydrochloric acid and sodium hydroxide.



- (iii) Gaseous reactions where the number of moles of reactants and products is the same, that is, $\Delta n_g = 0$

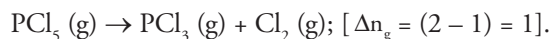


In the above reaction $\Delta n_g = 0$,

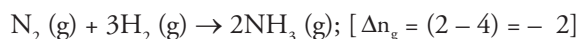
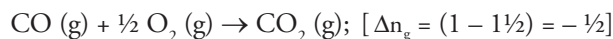
Therefore, $\Delta H = \Delta E + \Delta n_g RT = \Delta E + 0 \times RT = \Delta E$.

When $\Delta n_g \neq 0$, ΔH and ΔE will have different values.

- (i) When n_p is greater than n_r , then Δn_g is positive and $\Delta H > \Delta E$, for example,



- (ii) When n_p is lesser than n_r , then Δn_g is negative and $\Delta H < \Delta E$, for example,



Solved examples

1. If for the reaction. $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightarrow 2\text{NH}_3 (\text{g})$; the change in enthalpy ΔH is -92.38 kJ at 298 K . Find ΔE at 298 K .

Solution

$$\Delta H = \Delta E + \Delta n_g RT$$

For the reaction $\text{N}_2 (\text{g}) + 3\text{H}_2 (\text{g}) \rightarrow 2\text{NH}_3 (\text{g})$

$$\Delta n_g = 2 - 4 = -2 \text{ mol}; \quad T = 298 \text{ K}$$

$$\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Placing these values in the equation, we get

$$-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$$

$$-92380 = \Delta E - 4955$$

$$\Delta E = -92380 + 4955 = -87425 \text{ J} = -87.425 \text{ kJ}$$

2. Determine the difference between the heats of reaction at constant pressure and constant volume for the reaction at 25 °C in kJ



Solution

Heat of reaction at constant pressure (ΔH) and heat of reaction at constant volume (ΔE) are related as $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta H - \Delta E = \Delta n_g RT$$

$$\Delta n_g = 12 - 15 = -3; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; T = 298 \text{ K}$$

$$\Delta H - \Delta E = -3 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} = -7430 \text{ J} = -7.43 \text{ kJ}$$

Practice problems

1. The enthalpy changes for the following reaction at 298 K and 1 atm are given below



Calculate the internal energy change for the reactions.

[Ans (i) -874 kJ (ii) -1360.53 kJ]

2. The heat of combustion of gaseous methane (CH_4) at constant volume is measured with the help of a bomb calorimeter. It is found to be $-885.4 \text{ kJ mol}^{-1}$ at 298 K. Find the value of enthalpy change. [Ans -890.355 kJ]
3. The heat of combustion of C_2H_4 at 17 °C at constant volume is 332.190 kcal. Find the heat of combustion at constant pressure. [Ans -333.342 kcal mol⁻¹]

15.5 Heat Capacity

Heat capacity, denoted by 'C', is the capacity of a system to absorb heat and store energy. When heat is absorbed by the system, the temperature increases. These heat changes can occur at constant pressure or at constant volume. The amount of heat required to raise the temperature by 1 °C is called the **heat capacity**. If the temperature of 1 g of a substance is raised by 1 °C it is called **specific heat capacity**, and if the temperature of one mole of a substance is raised by 1 °C then it is termed as the **molar heat capacity**.

The heat capacity is not independent of temperature. If the temperature of the system is raised from T_1 to T_2 , the heat capacity of the system will have different values at different values of T_1 and T_2 . The *mean heat capacity* $\bar{C}(T_2, T_1)$ of a system between two temperatures T_2 and T_1 is defined as the amount of heat q , absorbed by the system to raise the temperature from T_1 to T_2 divided by the temperature difference. Thus,

$$\bar{C}(T_2, T_1) = \frac{q}{T_2 - T_1}$$

For the true heat capacity of the system at a given temperature, an infinitesimally small temperature difference should be taken. Thus, heat capacity is defined as

$$C = \frac{\delta q}{dT} \quad \dots (1) \tag{1}$$

The δ in δq represents that q is an inexact differential and is path-dependent. The heat change can be measured under conditions of either constant volume or constant pressure; consequently, heat capacity can also be determined at constant volume C_v and at constant pressure C_p .

(i) **Heat capacity at constant volume (C_v)**

From the first law of thermodynamics, we have

$$\delta q = dE - w \tag{2}$$

On substituting the value of δq in Eq. (1), we get

$$C = \frac{dE - PdV}{dT} \tag{3}$$

At constant volume, that is, when $dV = 0$, Eq. (3) becomes

$$C_v = \left(\frac{dE}{dT} \right)_v \quad \text{or} \quad \left(\frac{\partial E}{\partial T} \right)_v \tag{4}$$

Thus, the rate of change of internal energy with temperature is the heat capacity of the system at constant volume.

(ii) **Heat capacity at constant pressure (C_p)**

If the pressure is held constant, then there occurs an increase in volume and work is done by the system. By convention work done by the system is negative hence Eq. (2) becomes $\delta q = dE + PdV$. On substituting the value of δq in Eq. (1) we get

$$C_p = \frac{dE + PdV}{dT} \tag{5}$$

Heat content at constant pressure is defined as

$$H = dE + PdV \tag{6}$$

Substituting Eqs (6) in (5) we obtain,

$$C_p = \left(\frac{dH}{dT} \right)_p \quad \text{or} \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (7)$$

Hence, the rate of change of enthalpy with temperature is the heat capacity of the system at constant pressure.

15.6 The First Law of Thermodynamics and Ideal Gases

We will now discuss the behavior of ideal gas in light of the first law of thermodynamics. An ideal gas obeys the relationship

$$PV = nRT.$$

where n = number of moles of the gas, V = volume of the gas at pressure P and temperature T . R is the universal gas constant. Let us now study the behavior of ideal gases.

1. The internal energy of an ideal gas

If the internal energy, E , of an ideal gas is regarded as a function of V and T , then

$$E = f(V, T)$$

$$\text{and } dE = \left(\frac{\partial E}{\partial V} \right)_T dV + \left(\frac{\partial E}{\partial T} \right)_V dT \quad \dots(1) \quad (1)$$

$$\text{but } \left(\frac{\partial E}{\partial T} \right)_V = C_v, \text{ Inserting this value in Eq. (1), we get}$$

$$dE = \left(\frac{\partial E}{\partial V} \right)_T dV + C_v dT \quad \dots(2) \quad (2)$$

$$\text{From the first law of thermodynamics, } dE = \delta q + \delta w \quad (3)$$

On substituting the value of dE from Eq. (2) in Eq. (3) we get,

$$\begin{aligned} \delta q + \delta w &= \left(\frac{\partial E}{\partial V} \right)_T dV + C_v dT \\ \delta q &= \left(\frac{\partial E}{\partial V} \right)_T dV + C_v dT - \delta w \end{aligned} \quad (4)$$

For an ideal gas, Joule–Thomson effect should be zero (discussed in Section 15.12), and when an ideal gas expands there is no absorption or evolution of heat, provided no external work is done, that is, if $\delta w = 0$ then $\delta q = 0$. Inserting these conditions in Eq. (4) we get

$$\begin{aligned} 0 &= \left(\frac{\partial E}{\partial V} \right)_T dV + C_v dT + 0 \quad \text{or} \\ \left(\frac{\partial E}{\partial V} \right)_T dV + C_v dT &= 0 \end{aligned}$$

At constant temperature $dT = 0$ then

$$\left(\frac{\partial E}{\partial V}\right)_T dV = 0$$

Since the volume is changing, dV is not equal to zero, hence

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad (5)$$

Thus, the rate of change of internal energy with volume at constant temperature is zero. As volume and pressure are interdependent, at constant temperature Eq. (5) can also be expressed as

$$\left(\frac{\partial E}{\partial P}\right)_T = 0 \quad (6)$$

Thus, the rate of change of internal energy with pressure or volume at constant temperature is zero. From Eq. (5) and Eq. (6), it is evident that internal energy of an ideal gas is a function of temperature only.

Thermodynamically, an ideal gas is one that fulfills the following conditions

$$(i) \quad PV = nRT$$

$$(ii) \quad \left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \text{or} \quad \left(\frac{\partial E}{\partial P}\right)_T = 0$$

2. Enthalpy of an ideal gas

The enthalpy of an ideal gas is related to the internal energy by the relation

$$H = E + PV.$$

On differentiating with respect to V at constant temperature we get,

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T + \left(\frac{\partial(PV)}{\partial V}\right)_T$$

For an ideal gas $\left(\frac{\partial E}{\partial V}\right)_T = 0$. Further PV remains constant at constant temperature, hence $\left(\frac{\partial(PV)}{\partial V}\right)_T = 0$

$$\text{Consequently, } \left(\frac{\partial H}{\partial V}\right)_T = 0 \quad (7)$$

Similarly, it can be shown that $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

Hence, enthalpy of an ideal gas is a function of temperature only.

3. Heat capacity of an ideal gas at constant pressure and constant volume

As discussed earlier (Section 15.5), the heat capacity of an ideal gas at constant volume and constant pressure are given by

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

As discussed above, for an ideal gas, E is independent of V , and H is independent of P , the subscripts v and p may be removed implying the conditions of constant volume and constant pressure and expressions may be rewritten as

$$C_v = \frac{dE}{dT} \quad \text{or} \quad dE = C_v dT \quad (8)$$

$$C_p = \frac{dH}{dT} \quad \text{or} \quad dH = C_p dT \quad (9)$$

4. Relation between C_p and C_v for an ideal gas

We know that

$$H = E + PV.$$

By partial differentiation,

$$dH = dE + PdV + VdP.$$

At constant pressure, $VdP = 0 \therefore dH = dE + PdV$

Differentiating the above equation with respect to T at constant pressure, we have

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial E}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p \quad (1)$$

We know that $E = f(V, T)$

By rules of partial differentiation, $dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$

On dividing this equation by dT , keeping pressure constant, we get

$$\left(\frac{\partial E}{\partial T}\right)_p = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_V \quad (2)$$

Substituting Eq. (2) in Eq. (1), we get

$$\begin{aligned} \left(\frac{\partial H}{\partial T}\right)_p &= \left[\left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_V\right] + P\left(\frac{\partial V}{\partial T}\right)_p \\ \therefore \left(\frac{\partial H}{\partial T}\right)_p &= C_p \quad \text{and} \quad \left(\frac{\partial E}{\partial T}\right)_V = C_v \\ \therefore C_p &= C_v + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \quad (3)$$

For an ideal gas, we get

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \text{and} \quad P\left(\frac{\partial V}{\partial T}\right)_p = R$$

Therefore, Eq. (3) becomes

$$C_p = C_v + R \quad \text{or} \quad C_p - C_v = R.$$

15.7 Isothermal Processes in Ideal Gases

We know that the internal energy of an ideal gas depends only on temperature; hence, if the temperature does not change there will be no change in internal energy, that is, $\Delta E=0$. If an ideal gas expands isothermally, then according to the first law of thermodynamics,

$$dE = q + w = 0$$

$$\text{or} \quad q = -w$$

Thus, in an isothermal expansion, the gas does work at the cost of the heat absorbed. Like ΔE , the enthalpy change, ΔH in an isothermal process will also be zero. This can be proved as follows:

By definition, $H = E + PV$.

$$\text{or} \quad \Delta H = \Delta E + \Delta(PV) \tag{1}$$

At constant temperature, $\Delta E = 0$

$$PV = \text{constant.}$$

$$\therefore \Delta(PV) = 0$$

Substituting these values in Eq. (1), we get

$$\Delta H = 0.$$

Isothermal reversible expansion of an ideal gas

If the expansion is reversible, then the work done by the gas is given by

$$w = - \int_{V_1}^{V_2} P dV$$

For an ideal gas $P = \frac{nRT}{V}$, hence

$$\begin{aligned} w &= - \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \end{aligned}$$

$$\text{or} \quad w = -nRT \ln \left(\frac{V_2}{V_1} \right) = -2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right) \tag{2}$$

From Boyle's law,

$$P_1 V_1 = P_2 V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Thus, Eq. (2) can be written as,

$$w = -nRT \ln \left(\frac{P_1}{P_2} \right) = -2.303 nRT \log_{10} \left(\frac{P_1}{P_2} \right) \quad (3)$$

During expansion $V_2 > V_1$ and $P_1 > P_2$ hence the work comes out to be negative which is in conformity with the sign convention.

As for an ideal gas, the heat absorbed in isothermal reversible expansion is equal to the work done by the gas; hence,

$$q = 2.303 nRT \log_{10} \left(\frac{P_1}{P_2} \right) = 2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right) \quad (4)$$

Isothermal irreversible expansion of an ideal gas

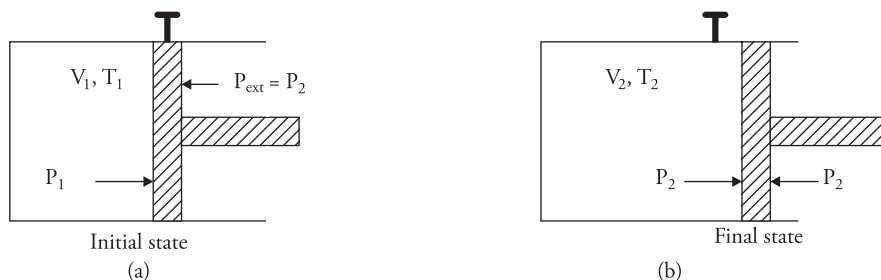


Figure 15.4 Irreversible expansion of an ideal gas against a constant pressure

(a) Initial state with piston held in place by a pin ($P_1 > P_2$)

(b) Final state when P_1 has fallen to match P_2 and $P_1 = P_2$

Let us consider a gas enclosed in a cylinder. The initial and final states of the system are shown in Fig. 15.4(a) and (b).

A given amount of ideal gas is placed in a cylinder fitted with a piston held in position by a pin. The initial volume and pressure of the gas are V_1 and P_1 , respectively. The internal pressure is greater than the external pressure. The pressure is released suddenly to a final pressure P_2 and then the gas expands against the final pressure P_2 .

Work done w Work done on the system is given by

$$\begin{aligned} w &= - \int_{V_1}^{V_2} P_{\text{ext}} dV = - \int_{V_1}^{V_2} P_2 dV = -P_2 \int_{V_1}^{V_2} dV \\ &= -P_2 (V_2 - V_1) = -P_{\text{ext}} \Delta V \end{aligned}$$

The work done by the gas during expansion is $(-w)$. Therefore,

$$(-w) = P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

$$\text{or } (-w) = nRT \left(1 - \frac{P_2}{P_1} \right) \quad \text{if } P_2 = P_{\text{ext}}$$

The work done on the system due to compression in an irreversible process will be different in magnitude and sign than the work of irreversible expansion.

$$\begin{aligned} w_{\text{irr}} &= -P_1(V_2 - V_1) = -P_1 \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) \\ &= nRT \left(1 - \frac{P_1}{P_2} \right) \end{aligned}$$

In compression $V_2 < V_1$; hence, w is positive, as P_2 and P_1 are different; hence, the two works are different.

Energy change ΔE :

For an ideal gas at constant temperature

$$\Delta E = E_2 - E_1 = 0$$

Heat change q :

$$q = \Delta E - w = 0 - w$$

$$\text{or } q = -w = P_2 \Delta V$$

$$= P_2(V_2 - V_1) = nRT \left[1 - \frac{P_2}{P_1} \right]$$

Enthalpy change ΔH :

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(RT)$$

$$\Delta H = 0 + 0 = 0 \quad [\text{Since } \Delta E = 0; \Delta(RT) = 0]$$

15.8 Adiabatic Processes in Ideal Gases

In an adiabatic process, there is no exchange of heat between the system and the surrounding, that is, $\Delta q = 0$.

Applying this condition in the first law expression,

$$\Delta E = q + w; \text{ we get}$$

$$\Delta E = 0 + w \quad \text{or}$$

$$w = \Delta E.$$

From the above equation, we see that both w and ΔE are positive which means that work done on the system increases the internal energy of the system and the temperature increases. If both w

and ΔE are negative, it implies that work done by the system decreases the internal energy of the system, consequently the temperature falls or we can say that adiabatic expansion is accompanied by a decrease in temperature and adiabatic compression by an increase in temperature.

Temperature–volume, temperature–pressure and pressure–volume relationship in the reversible adiabatic expansion of an ideal gas

Consider n moles of an ideal gas that occupies a volume V at a pressure P . If the gas expands under reversible conditions, the pressure P can be taken as the confining pressure. For an infinitesimal increase in volume, dV , the work done by the gas is given by

$$dw = -PdV$$

In case of an adiabatic expansion $-dw = -dE$

$$\therefore dE = -PdV \quad (1)$$

As studied earlier for n moles of an ideal gas

$$dE = nC_v dT \quad (2)$$

Substituting in Eq. (1) we get

$$nC_v dT = -PdV \quad (3)$$

also for an ideal gas

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

Substituting the value of P in Eq. (3), we get

$$nC_v dT = -\frac{nRT}{V} dV$$

$$\text{or} \quad C_v \frac{dT}{T} = -R \frac{dV}{V} \quad (4)$$

If the volume changes from V_1 to V_2 and the temperature from T_1 to T_2 , then by integrating Eq. (4) within limits, we get

$$\int_{T_1}^{T_2} C_v \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or} \quad C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\text{or} \quad C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$$

$$\left(\ln \frac{T_2}{T_1} \right)^{C_v} = \left(\ln \frac{V_1}{V_2} \right)^R$$

Taking antilogarithm, we get

$$\left(\frac{T_2}{T_1}\right)^{C_v} = \left(\frac{V_1}{V_2}\right)^R$$

or
$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} = \left(\frac{V_1}{V_2}\right)^{\frac{C_p - C_v}{C_v}} = \left(\frac{V_1}{V_2}\right)^{\frac{C_p}{C_v} - 1}$$

Putting γ for $\frac{C_p}{C_v}$ we obtain

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \quad (5)$$

$$\text{or } T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \quad (6)$$

$$\text{or } TV^{\gamma - 1} = \text{constant} \quad (7)$$

Relation between Temperature and Pressure

For an ideal gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{V_1}{V_2} = \frac{P_2 T_1}{P_1 T_2}$$

Substituting in Eq. (5), we get

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2 T_1}{P_1 T_2}\right)^{\gamma - 1}$$

or
$$\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma - 1} \quad (8)$$

Relation between Pressure and Volume

Again consider the relation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

Substituting in Eq. (5), we get

$$\left(\frac{P_2 V_2}{P_1 V_1} \right) = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\text{or} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\text{or} \quad PV^{\gamma} = \text{constant} \quad (9)$$

Work done under adiabatic reversible conditions

$\Delta E = q + w$ ∴ for an adiabatic process $q = 0$

Hence $\Delta E = w$

$$w = nC_v(T_2 - T_1)$$

$$= nC_v T_1 \left(\frac{T_2}{T_1} - 1 \right)$$

$$\text{but } \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{R}{C_v}} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$w = nC_v T_1 \left(\left(\frac{V_1}{V_2} \right)^{\frac{R}{C_v}} - 1 \right)$$

For work expansion, that is, work done by the system $V_2 > V_1$ the work will be negative; for work of compression, that is, work done on the system $V_2 < V_1$ hence the work done will be positive.

Work done in an adiabatic process can also be expressed in terms of T and P ,

$$\text{Then } w = nC_v(T_2 - T_1) = nC_v T_1 \left(\frac{T_2}{T_1} - 1 \right)$$

$$\text{As studied earlier - } \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{R}{C_p}} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

$$\therefore w = nC_v T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

In terms of P and V , the work is expressed as

$$w = nC_v(T_2 - T_1)$$

$$\text{but } P_1 V_1 = nRT_1 \quad \text{and } P_2 V_2 = nRT_2, \text{ we get}$$

$$w = \frac{nC_v}{nR}(P_2V_2 - P_1V_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$$

$$\text{Since } \frac{C_v}{R} = \frac{C_v}{C_p - C_v} = \frac{1}{\gamma - 1}$$

Adiabatic free expansion (irreversible work)

In irreversible work when the gas expands against vacuum, that is, in the absence of external pressure the work done will be zero. Hence from the first law of thermodynamics

$$\Delta E = q + w = 0 + 0 = 0$$

$$\text{also } \Delta E = C_v(T_2 - T_1) = 0$$

$$\therefore T_1 = T_2 \text{ and } \Delta H = C_p(T_2 - T_1) = 0 \text{ as } T_1 = T_2$$

Thus for adiabatic free expansion of an ideal gas all the quantities w , q , ΔE and ΔH are zero.

Adiabatic Irreversible Expansion

Work done: In an irreversible expansion the external pressure is constant and the work of expansion is given by

$$\begin{aligned} (-w_{\text{irr}}) &= \int_{V_1}^{V_2} P_{\text{ext}} dV = P_{\text{ext}}(V_2 - V_1) \\ &= P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) \end{aligned}$$

if $P_{\text{ext}} = P_2 =$ the final pressure, then

$$(-w_{\text{irr}}) = P_2 \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) = nRT_1 \left(\frac{T_2}{T_1} - \frac{P_2}{P_1} \right)$$

Here T_2 is the final temperature in adiabatic irreversible expansion and is different than that in the adiabatic reversible expansion.

Energy change:

Since $q = 0$ for adiabatic changes, the first law equation gives

$$\Delta E = w = -P_2(V_2 - V_1) = nC_v(T_2 - T_1)$$

$$= P_2 \left(\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2} \right)$$

$$\text{or } C_v(T_2 - T_1) = RT_1 \left(\frac{P_2}{P_1} \right) - RT_2$$

$$\text{or } (C_v + R)T_2 = [C_v + R(P_2 / P_1)]T_1$$

$$\therefore T_2 = \left(\frac{C_v + R(P_2 / P_1)}{C_p} \right) T_1$$

Enthalpy change :

$$\Delta H = C_p(T_2 - T_1)$$

Using the value of T_2 calculated from above equation ΔE and ΔH can be calculated.

Comparison of isothermal and adiabatic expansion of an ideal gas

The pressure-volume curves of isothermal and adiabatic expansions are illustrated in Figure (15.5). In an adiabatic expansion, $PV^\gamma = \text{constant}$ and in isothermal expansion, $PV = \text{constant}$. As the value of γ is always greater than unity, for a given decrease in pressure, the increase in volume would be lesser in case of adiabatic expansion. Hence, the adiabatic P-V curve will be steeper than the isothermal P-V curve.

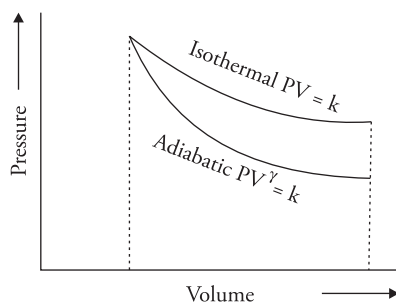


Figure 15.5 Isothermal and adiabatic expansions of an ideal gas

The smaller volume change can be explained by the fact that in the adiabatic expansion, the internal energy decreases and consequently the temperature falls. This cooling effect leads to the shrinking in volume. In an isothermal expansion, the temperature remains constant. As work of expansion is equal to the area under the curve, it is evident from the figure that the work done by the ideal gas is greater in isothermal expansion than in adiabatic expansion.

Solved examples

- 2 moles of an ideal gas at 20 °C is allowed to expand adiabatically and reversibly from 15 to 5 atm. Calculate the final volume and temperature for this gas. $C_p = 8.58 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

Solution

Since $C_p = 8.58 \text{ cal mol}^{-1} \text{ deg}^{-1}$

$$C_v = C_p - R = 8.58 - 1.987 = 6.593 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{8.58}{6.593} = 1.301$$

we know that

$$\left(\frac{T_2}{T_1} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{\gamma-1}$$

$$\text{Here } P_1 = 15 \text{ atm; } P_2 = 5 \text{ atm; } T_1 = 273 + 20 = 293 \text{ K } \gamma = 1.301$$

$$\therefore \left(\frac{T_2}{293} \right)^{1.301} = \left(\frac{5}{15} \right)^{1.301-1}$$

$$\text{or } T_2 = 293 \times \left(\frac{5}{15} \right)^{\frac{0.301}{1.301}} = 227.23 \text{ K}$$

$$= 227.2 - 273 = -45.77^\circ \text{C}$$

$$\therefore \text{Final temperature} = -45.77^\circ \text{C}$$

The final volume V_2 is given by

$$V_2 = \frac{nRT_2}{P_2};$$

here $T_2 = 273 - 45.77 = 227.23 \text{ K}$; $P_2 = 5 \text{ atm}$; $n = 2 \text{ moles}$, $R = 0.082 \text{ L atm deg}^{-1} \text{ mol}^{-1}$

$$V_2 = \frac{2 \text{ mol} \times 0.082 \text{ L atm deg}^{-1} \text{ mol}^{-1} \times 227.23 \text{ K}}{5 \text{ atm}}$$

$$V_2 = 7.45 \text{ L}$$

\therefore The final volume $V_2 = 7.45 \text{ L}$

2. Two moles of an ideal gas ($C_p = \frac{7}{2}R$) is allowed to expand adiabatically and reversibly at 27°C from a pressure of 10 atm to a pressure of 1 atm. Calculate the final temperature of the gas and the amount of work done by the gas.

Solution

$$\text{Since } C_p = \frac{7}{2}R$$

$$C_v = C_p - R = \frac{7}{2}R - R = \frac{5}{2}R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

For an adiabatic expansion of an ideal gas

$$\left(\frac{T_2}{T_1} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{\gamma-1}$$

Here $P_1 = 10 \text{ atm}$; $P_2 = 1 \text{ atm}$; $T_1 = 273 + 27 = 300 \text{ K}$ $\gamma = 1.4$

$$\therefore \left(\frac{T_2}{300} \right)^{1.4} = \left(\frac{1}{10} \right)^{1.4-1}$$

$$\begin{aligned} \text{or } T_2 &= 300 \times \left(\frac{1}{10} \right)^{\frac{0.4}{1.4}} = 155.38 \text{ K} \\ &= 155.3 - 273 = -117.61^\circ \text{C} \end{aligned}$$

Therefore, final temperature of the gas $T_2 = -117.61^\circ\text{C}$.

The work done by the gas in a reversible adiabatic expansion is given by

$$w = nC_v T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

$$n = 2, \quad C_v = \frac{5}{2}R, \quad T_1 = 300 \text{ K} \quad \gamma = 1.4 \quad P_2 = 1 \text{ atm} \quad P_1 = 10 \text{ atm}$$

$$w = 2 \times \frac{5}{2} \times 1.987 \times 300 \left(\left(\frac{1}{10} \right)^{\frac{1.4-1}{1.4}} - 1 \right) = -1436.79 \text{ cal}$$

Negative sign indicates the work expansion.

3. 4 mole of an ideal gas ($C_v = 6.593$) at 20°C and 15 atm is allowed to expand against a constant pressure of 5 atm adiabatically. Calculate (a) the final temperature of the gas, (b) the work done by the gas, (c) ΔE and (d) ΔH .

Solution

- (a) The final temperature of an adiabatic irreversible expansion is given by

$$T_2 = \frac{T_1}{C_p} \left(C_v + R \frac{P_2}{P_1} \right)$$

$$T_1 = 273 + 20 = 293 \text{ K}, \quad C_v = 6.593 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

$$C_p = C_v + R = 6.593 + 1.987 = 8.58 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

$$P_2 = 5 \text{ atm}; \quad P_1 = 15 \text{ atm}, \quad R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$T_2 = \frac{293}{8.58} \left(6.593 + 1.987 \times \frac{5}{15} \right) = 247.76 \text{ K}$$

$$= (247.76 - 273) = -25.23^\circ\text{C}$$

- (b) Work done by the gas

$$w = nC_v (T_2 - T_1)$$

$$w = 4 \times 6.593 \times (247.76 - 293)$$

$$w = -4 \times 6.593 \times 45.24 = -1193.06 \text{ cal} \text{ (negative sign indicates work done by the gas)}$$

In an adiabatic process, $\Delta E = w = 1193.06 \text{ cal}$

$$\Delta H = \Delta E + P\Delta V$$

$$\text{or } \Delta H = \Delta E + nR\Delta T.$$

$$\Delta H = -1193.06 + 4 \times 1.987 (247.76 - 293)$$

$$\Delta H = -1193.06 - 359.56 = -1552.62 \text{ cal}$$

4. A rubber balloon filled with an ideal gas ($\gamma = 1.4$) at a pressure of 2 atm and 27 °C suddenly bursts in a room where the atmospheric pressure is 1 atm. Calculate the resulting drop of temperature.

Solution

When the gas is released suddenly it does not get any time to absorb heat and hence its temperature drops. Also the gas is expanding against a constant pressure at 1 atm. Thus, the given process comes under the category of irreversible adiabatic expansion of gas

For an irreversible adiabatic expansion, the final temperature is given by

$$T_2 = \frac{T_1}{C_p} \left(C_v + R \frac{P_2}{P_1} \right)$$

$$T_1 = 273 + 27 = 300 \text{ K}$$

$$P_2 = 1 \text{ atm}; \quad P_1 = 2 \text{ atm}, \quad \gamma = 1.4$$

The values of C_p and C_v can be calculated as follows:

$$\frac{C_p}{C_v} = \gamma$$

$$\text{or } \frac{C_p}{C_v} - 1 = \gamma - 1$$

$$\frac{C_p - C_v}{C_v} = \gamma - 1$$

$$\text{or } \frac{R}{C_v} = \gamma - 1, \quad ,$$

$$\text{or } C_v = \frac{R}{\gamma - 1} = \frac{1.987}{1.4 - 1} = 4.967$$

$$\therefore C_p = C_v + R = 4.967 + 1.987 = 6.954$$

Substituting these values, we get

$$T_2 = \frac{300}{6.954} \left(4.967 + 1.987 \times \frac{1}{2} \right)$$

$$T_2 = 257.1 \text{ K} = -15.9 \text{ }^\circ\text{C}$$

Thus, the final temperature is 15.9 °C.

Practice problems

1. A certain volume of dry gas is expanded to three times its volume adiabatically. Calculate the final pressure and temperature assuming ideal behavior of the gas ($\gamma = 1.4$).

[Ans $T = 176 \text{ K}$; $P = 163.2 \text{ mm}$]

2. 5 moles of a monoatomic ideal gas is compressed reversibly and adiabatically. The initial volume is 6 dm^3 and the final volume is 2 dm^3 . The initial temperature is 27°C .
- (i) What would be the final temperature in this process?
- (ii) Calculate w , q and ΔE for the process. Given $C_v = 20.91 \text{ J K}^{-1} \text{ mol}^{-1}$, $\gamma = 1.4$
- [Ans $T_2 = 465.55 \text{ K}$; $w = -3378.87 \text{ J}$; $q = 0$; $\Delta E = 3378.87 \text{ J}$]
3. 1.6 mole of an ideal gas ($C_v = 2.5 R$) at 300 K is allowed to expand adiabatically from 5 atm to a final pressure of 2 atm against a constant external pressure of 1 atm . Calculate q , w , ΔE and ΔH .
- [Ans $T_2 = 270 \text{ K}$; $q = 0$; $\Delta E = w = -997.68 \text{ J}$; $\Delta H = -1396.7 \text{ J}$]
4. 2 moles of an ideal gas ($C_v = 2.5 R$) is maintained in a volume of 11.2 dm^3 at 273 K . The temperature of the gas is raised to 373 K at (i) constant volume and (ii) at constant pressure. Calculate w , q , ΔE and ΔH for the two cases separately.
- [Ans At constant volume $w = 0$; $q_v = \Delta E = 4157 \text{ J}$; $\Delta H = 5819.8 \text{ J}$
At constant pressure, $w = 1662.8 \text{ J}$; $\Delta E = 4157 \text{ J}$; $(q_p) = \Delta H = 5819.8 \text{ J}$]
5. 1.0 mole of an ideal gas ($C_p = 2.5 R$) at 1 atm and 273 K undergoes a change reversibly so that the volume is doubled. The nature of the process is unspecified but enthalpy change is $2078.5 \text{ J mol}^{-1}$ and heat absorbed is 1675 J mol^{-1} . Calculate the final temperature, pressure, w and ΔE for the process.
- [Ans $T_2 = 373 \text{ K}$; $\Delta E = 1247.1 \text{ J mol}^{-1}$; $q = 427.9 \text{ J mol}^{-1}$; $P_2 = 0.683 \text{ atm}$]

15.9 Applications of First Law of Thermodynamics

1. Enthalpies of reactions

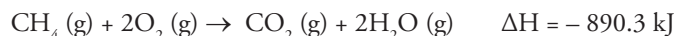
One of the important applications of the first law of thermodynamics is the calculation of enthalpies of reaction.

The enthalpy of reaction is the enthalpy change (amount of heat evolved or absorbed) when the moles of reactants and products as indicated by a balanced chemical equation react completely.

Mathematically,

$$\Delta H = \text{Enthalpy of product} - \text{Enthalpy of reactant.}$$

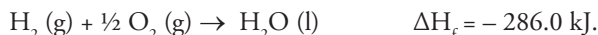
For example, 1 mole of methane reacts with two moles of oxygen to form one mole of carbon dioxide and two moles of water. The enthalpy change is -890.3 kJ



If the reaction occurs at 1 atmospheric pressure and 298 K temperature, then the heat change accompanying the reaction is referred to as the standard enthalpy of reaction and is represented by ΔH° where the superscript $^\circ$ indicates the standard state.

2. **Enthalpy of formation (ΔH_f)** It is the change in enthalpy when one mole of a compound (in its standard state) is formed from its elements (in their standard states).

For example,



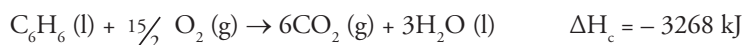
3. **Heat of combustion or enthalpy of combustion (ΔH_c)** It is the heat change when one mole of a substance is burnt completely in excess of oxygen or air.

Some examples are given below

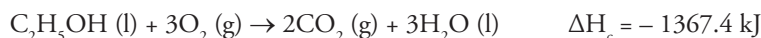
- (i) Combustion of carbon



- (ii) Combustion of benzene



- (iii) Combustion of ethyl alcohol



It may be noted that the heat of combustion is always negative because heat is always evolved during combustion.

4. **Heat of solution or enthalpy of solution (ΔH_{sol})**

When a solute is dissolved in a solvent, heat is either absorbed or given out. The heat change when one mole of a solute is dissolved in a specified quantity of the solvent at a given temperature is defined as the heat of solution at that temperature. For example,

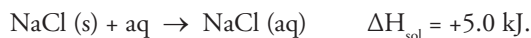
When one mole of ammonium nitrate is dissolved in 1 L of water to prepare a 1 M solution, 26.0 kJ of heat is absorbed. It may be expressed as



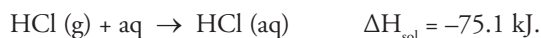
If a substance is dissolved in large excess of the solvent, then there is no additional change in heat on further dilution. This is called the heat of solution at infinite dilution and can be defined as the heat change on dissolving 1 mole of a solute in large excess of the solvent such that further dilution does not produce any additional heat change.

For example,

- (i) Dissolution of sodium chloride



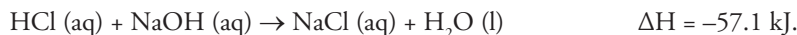
- (ii) Dissolution of hydrochloric acid



5. **Heat or enthalpy of neutralisation** At a given temperature, enthalpy of neutralisation is defined as the change in enthalpy of the system when 1 g equivalent of an acid is completely neutralised by 1 g equivalent of a base or vice versa in dilute solution

Example

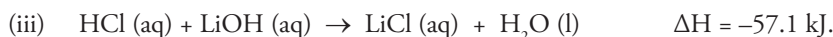
- (i) Neutralisation of HCl with NaOH



- (ii) Neutralisation of HNO_3 with NaOH



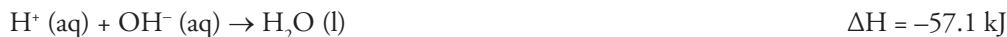
Similarly,



It may be noted that the heat of neutralisation of a strong base by strong acid is always equal to -57.1 kJ irrespective of the nature of acid or base. This is because heat of neutralisation is in fact the heat of formation of 1 mole of water from 1 g equivalent of H^+ (of acid) and 1 g equivalent of OH^- (of base), while the other ions of the strong acid and base remain unaltered.



Cancelling the common ions,



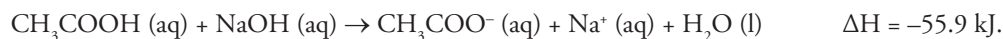
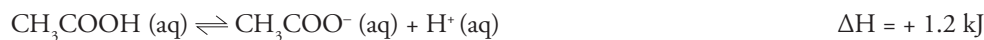
However, the heat of neutralisation of weak acid or weak base is less than 57.1 kJ and also depends on the weak acid or base. For example,



This is because the weak acids and weak bases are not completely dissociated at all concentrations. Hence, the neutralisation involves not only the combination of H^+ and OH^- but also the dissociation of the weak acid or base. As the dissociation is an endothermic process heat is consumed in it. Hence, heat of neutralisation for a weak acid and weak base is the sum of heat evolved by the combination of H^+ and OH^- and the heat required for the dissociation of the weak acid and base. For example,



Strong base



6. **Enthalpy (or heat) of fusion** Enthalpy of fusion is the heat change associated with the conversion of 1 mole of a solid substance into its liquid state at its melting point.

For example, when one mole of ice melts at 0 °C (or 273 K), the heat absorbed is 6.0 kJ. This corresponds to the process



7. **Enthalpy (or heat) of vaporisation** Enthalpy of vaporisation is the heat change accompanying the conversion of 1 mole of a liquid into gaseous state at its boiling point.

For example, the heat required to vaporise 1 mole of water (liquid) into gas (steam) at 100 °C (373 K) is 40.6 kJ. This is represented as



8. **Enthalpy (or heat) of sublimation** Enthalpy of sublimation is the heat change during the conversion of one mole of a solid directly into its gaseous state at a temperature below its melting point. For example, heat of sublimation of iodine.



15.10 Laws of Thermochemistry

On the basis of the principles of conservation of energy, two important laws of thermochemistry were formulated

- (1) Lavoisier and Laplace's law
 - (2) Hess's law of constant heat summation.
1. **Lavoisier and Laplace's law** It was given by Lavoisier and Laplace in 1780, which states that_ 'The amount of heat supplied to decompose a compound into its elements is equal to the amount of heat released when that compound is formed from its elements'.

In other words,

Heat of formation = Heat of decomposition of a compound but of opposite sign.

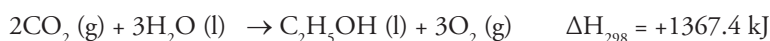
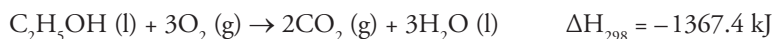
Thus, larger the heat of formation of a compound, the greater will be its stability.

The importance of this law is that the thermochemical equations can be reversed, provided the sign of ΔH is changed. Thus,



This law applies to all types of reactions

For example,



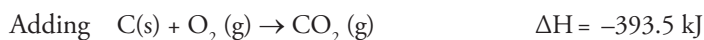
2. **Hess's law of constant heat summation** We know that ΔH and ΔE are state functions, that is, their value depends only on the initial and final states of the system and not on the path followed. On the basis of this, G.H. Hess in 1840 proposed an important generalisation that may be stated as follows: If a chemical reaction occurs in one or two or more steps then the total heat evolved or absorbed will be the same irrespective of the number of steps in which the reaction is taking place.

The law can be illustrated by considering the example of the formation of carbon dioxide from carbon and oxygen. Carbon can be converted in CO_2 in two ways

Path I (in one step)



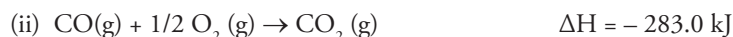
Path II (in two steps)



Applications of Hess's law

It may be noted that the thermochemical equations can be added, subtracted, divided or multiplied by an integer like algebraic equations. The terms identical in quality and quantity on both sides of the equation may be cancelled. This helps in computing indirectly the heat of formation, heat of reaction, heat of transition, etc that cannot be measured experimentally.

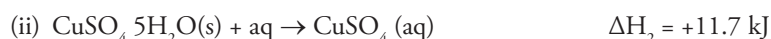
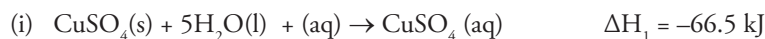
1. **Determination of heat of formation** Compounds like methane (CH_4), carbon monoxide (CO) and benzene (C_6H_6) cannot be prepared directly by the combination of their elements. Therefore, experimental determination of their heats of formation is not possible. The heats of formation of such substances can be determined indirectly with the help of Hess's law. For example,



Subtracting Eq. (ii) from Eq. (i) we get



2. **Calculation of heat of hydration** Hydration reaction can be either endothermic or exothermic. The heat change associated with the hydration of one mole of an anhydrous salt is termed as its heat of hydration. For example, the heat of hydration of CuSO_4 can be calculated from the knowledge of the heat of solution of its anhydrous salt and hydrated salt.

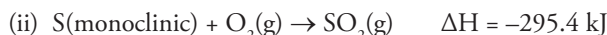


Subtracting Eq. (ii) from Eq. (i) we get



3. **Determination of heat of transition** Allotropic modifications like transition of graphite to diamond, rhombic sulphur to monoclinic sulphur, yellow phosphorus to red phosphorus, etc are accompanied by heat change. These heat changes can be calculated with the help of Hess's law.

For example, the heats of combustion of rhombic and monoclinic sulphur are as follows:



Subtracting Eq. (ii) from (i) we get,

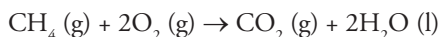


Thus the heat of transition of rhombic sulphur to monoclinic sulphur is 4.0 kJ.

4. **Prediction of heats of various reactions** Hess's law helps in calculating the enthalpies of those reactions whose enthalpies cannot be determined directly.

Solved examples

1. Calculate the standard enthalpy change for the reaction



The standard enthalpies of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are $-74.8 \text{ kJ mol}^{-1}$, -393.5 and $285.8 \text{ kJ mol}^{-1}$, respectively.

Solution

The standard enthalpy change for the reaction, ΔH° is given by

$$\begin{aligned} \Delta H^\circ &= \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants}) \\ &= \{ \Delta H_f^\circ[\text{CO}_2(\text{g})] + 2\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] \} - \{ \Delta H_f^\circ[\text{CH}_4(\text{g})] + 2\Delta H_f^\circ[\text{O}_2(\text{g})] \} \end{aligned}$$

$$\Delta H_f^\circ[\text{CH}_4(\text{g})] = -74.8 \text{ kJ mol}^{-1} \quad ; \quad \Delta H_f^\circ[\text{CO}_2(\text{g})] = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1} \quad ; \quad \Delta H_f^\circ[\text{O}_2(\text{g})] = 0 \text{ (by convention)}$$

$$\Delta H^\circ = [(-393.5) + 2(-285.8)] - [(-74.8) + 2 \times 0]$$

$$= -965.1 + 74.8 = -890.3 \text{ kJ mol}^{-1}$$

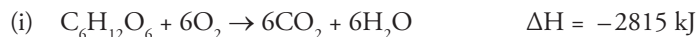
2. Calculate the enthalpy of formation of glucose from the following data.

Enthalpies of combustion of glucose, carbon and hydrogen are -2815 kJ, -394 kJ and -286 kJ, respectively.

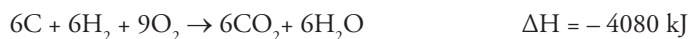
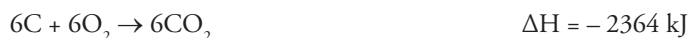
Solution

To find ΔH for the reaction, $6C + 6H_2 + 3O_2 \rightarrow C_6H_{12}O_6$; $\Delta H = ?$

Given



Multiply Eq. (ii) by 6 and Eq. (iii) by 6 and add



Subtracting Eq. (i) from the above equation,



Thus, ΔH_f of $C_6H_{12}O_6$ is -1265 kJ.

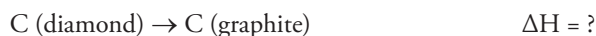
3. The enthalpies of combustion of diamond and graphite are -395.4 kJ and -393.5 kJ, respectively. Calculate the enthalpy of transformation from diamond to graphite.

Solution

The enthalpies of combustion may be represented as



The enthalpy change for the following transformation is desired



This can be obtained by subtracting Eq. (ii) from Eq. (i)

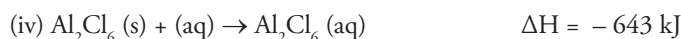
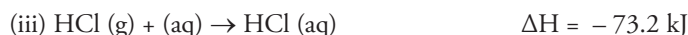
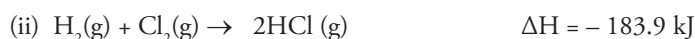
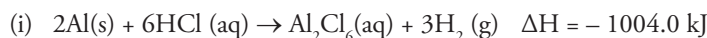




$$[\text{Ans} = \Delta H = -1.9 \text{ kJ}]$$

Practice problems

1. Calculate the enthalpy of formation of anhydrous aluminium chloride Al_2Cl_6 from the following data



$$[\text{Ans} -1351.9 \text{ kJ}]$$

2. If the heat of combustion of C_2H_2 , C (graphite) and H_2 are $-1300 \text{ kJ mol}^{-1}$, -395 kJ mol^{-1} and -286 kJ mol^{-1} , respectively, calculate the standard heat of formation of acetylene.

$$[\text{Ans} \quad \Delta H_f^0 \text{ for } \text{C}_2\text{H}_2 (\text{g}) = 224 \text{ kJ}]$$

3. Calculate the standard enthalpy of formation of propane (C_3H_8) if its enthalpy of combustion is $-2220 \text{ kJ mol}^{-1}$. The enthalpy of formation of $\text{CO}_2 (\text{g})$ and $\text{H}_2\text{O (l)}$ are -393.5 and $-285.8 \text{ kJ mol}^{-1}$, respectively.

$$[\text{Ans} -103.5 \text{ kJ}]$$

15.11 Kirchhoff's Equation

The heat of a reaction varies with temperature. Kirchhoff in 1858 deduced a mathematical expression for defining the variation of heat of reaction with temperature. All these expressions are based on the first law of thermodynamics.

To deduce the Kirchhoff's equation, let us consider the reaction



Let H_A be the heat content of the reactant and H_B be the heat content of products at the same temperature and pressure, then

$$\Delta H = H_B - H_A$$

All the quantities are at the same pressure. Differentiating this equation with respect to temperature at constant pressure, we get

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = \left(\frac{\partial H_B}{\partial T} \right)_p - \left(\frac{\partial H_A}{\partial T} \right)_p$$

as we know $\left(\frac{\partial H}{\partial T}\right)_p$ is equal to C_p , hence -

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = (C_p)_B - (C_p)_A$$

$(C_p)_A$ and $(C_p)_B$ are the total heat capacities of the reactants and products, respectively, at a given (constant) pressure. The above equation can also be written as

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta C_p$$

This expression is generally known as the Kirchhoff's equation. Here, ΔC_p is equal to the difference in heat capacities of the products and reactants at constant pressure.

Heat capacity is an extensive property.

Consider a general chemical reaction,



the increase in heat capacity ΔC_p is given by

$$\Delta C_p = [l(C_p)_L + m(C_p)_M + \dots] - [a(C_p)_A + b(C_p)_B + \dots]$$

The above expression can be rewritten as

$$\Delta C_p = \sum (nC_p)_{\text{products}} - \sum (nC_p)_{\text{reactants}}$$

where n is the number of moles of each substance taking part in the reaction

$$\sum (nC_p)_{\text{products}} = \text{sum of molar enthalpies of the products.}$$

$$\sum (nC_p)_{\text{reactants}} = \text{sum of molar enthalpies of the reactants.}$$

Application of Kirchhoff's law

Kirchhoff's law helps in deducing the heat of reaction at one temperature if the heat of reaction at the other temperature is known. This can be done by integrating the Kirchhoff's equation between the temperature limits of T_1 and T_2 .

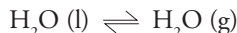
$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

ΔH_2 and ΔH_1 are the heats of reaction at the two temperatures. If we consider that C_p is constant and independent of temperature over a small temperature range, then ΔC_p is taken as the mean value $\overline{\Delta C_p}$ in the temperature range T_1 to T_2 .

$$\text{Hence, } \Delta H_2 - \Delta H_1 = \overline{\Delta C_p}(T_2 - T_1)$$

Solved examples

1. The enthalpy of evaporation of water at 373 K is 40.67 kJ mol⁻¹. What will be the enthalpy of evaporation at 353 K and 393 K if the average molar heats at constant pressure in this range for water in liquid and vapor states are 75.312 and 33.89 J K⁻¹ mol⁻¹, respectively.

Solution

Enthalpy change at 373 K, $\Delta H_1 = 40.67 \text{ kJ mol}^{-1} = 40670 \text{ J mol}^{-1}$.

According to Kirchhoff's equation,

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$$

$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$$

$$\begin{aligned}\Delta C_p &= \Delta C_{p, \text{H}_2\text{O(g)}} - \Delta C_{p, \text{H}_2\text{O(l)}} \\ &= 33.89 - 75.312 = -41.422\end{aligned}$$

Enthalpy of evaporation at 353 K

$$\begin{aligned}&= 40670 - 41.422(353 - 373) \\ &= 40670 + 41.422 \times 20 = 41498.44 \text{ J}\end{aligned}$$

Similarly enthalpy of evaporation at 393 K

$$= 40670 - 41.422(393 - 373) = 39841.56 \text{ J}$$

2. The heat of formation of one mole of HI from hydrogen and iodine vapor at 25 °C is 8000 cal.



Calculate the heat of formation at 10 °C and also the total change in the heat capacity at constant pressure. The molar heat capacities of hydrogen, iodine and HI vapor are given by the equations

$$C_p = 6.5 + 0.0017 T \quad \text{for Hydrogen (g).}$$

$$C_p = 6.5 + 0.0038 T \quad \text{for Iodine (g).}$$

$$C_p = 6.5 + 0.0016 T \quad \text{for HI (g)}$$

where T is the absolute temperature.

Solution

$$\Delta C_p = C_p(\text{HI}) - \frac{1}{2} [C_p(\text{H}_2) + C_p(\text{I}_2)].$$

$$= 6.5 + 0.0016T - \frac{1}{2} [6.5 + 0.0017T + 6.5 + 0.0038T].$$

$$= -0.00115T \text{ cal deg}^{-1}$$

Here,

$$\Delta H_{298} = \Delta H_{283} + \int_{283}^{298} \Delta C_p dT$$

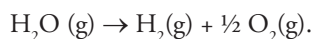
$$\text{where, } T_1 = 273 + 10 = 283 \text{ K} \quad T_2 = 273 + 25 = 298 \text{ K}$$

$$\text{also, } \Delta H_{298} = -8000 \text{ cal}$$

$$-8000 = \Delta H_{283} + \int_{283}^{298} (-0.00115)T \cdot dT$$

$$\begin{aligned} \Delta H_{283} &= -8000 + \frac{0.00115}{2} [T^2]_{283}^{298} \\ &= -8000 + \frac{0.00115}{2} [(298)^2 - (283)^2] \\ &= -7995 \text{ cal (approx)} \end{aligned}$$

3. Calculate ΔH at 25°C for the reaction



Given that ΔH at 18°C is $241.750 \text{ kJ mol}^{-1}$ and molar heat capacities expressed as $\text{J K}^{-1} \text{mol}^{-1}$ are

$$C_p(\text{H}_2) = 28.83, \quad C_p(\text{O}_2) = 29.12, \quad C_p(\text{H}_2\text{O}) = 33.56.$$

Solution

ΔC_p = Heat capacities of products – Heat capacities of reactants.

$$= \left[28.33 + \frac{1}{2} \times 29.12 \right] - 33.56 = 43.89 - 33.56 = 9.33 \text{ J K}^{-1} \text{mol}^{-1}$$

$$T_2 - T_1 = (273 + 25) - (273 + 18) = 7 \text{ K}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$$

$$\Delta H_1 \text{ at } 18^\circ\text{C} \text{ is } 241.750 \text{ kJ mol}^{-1} = 241750 \text{ J mol}^{-1}$$

$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1) = 241750 + 9.33 \times 7 = 241815.31 \text{ J mol}^{-1} = 241.815 \text{ kJ mol}^{-1}$$

Practice problems

1. ΔH of formation of $\text{H}_2\text{O (l)}$ is -68 kcal at 25°C . Calculate ΔH at 100°C , assuming the molar heat capacities of $\text{H}_2\text{(g)}$, $\text{O}_2\text{(g)}$ and $\text{H}_2\text{O (l)}$ to be 7.0 , 7.0 and 18.0 cal K^{-1} , respectively.
[Ans 67.44 kcal]
2. Find the heat required to raise the temperature of 1 mole of oxygen from 300 K to 1300 K at constant pressure?

$$C_p = 6.095 + 3.253 \times 10^{-3} T - 1.017 \times 10^{-6} T^2 \quad [\text{Ans } 7961.77 \text{ cal/mol}]$$

15.12 Joule–Thomson Effect

In the Joule–Thomson experiment, a gas was allowed to stream from a higher pressure P_1 to a lower pressure P_2 through a tube containing a throttle.

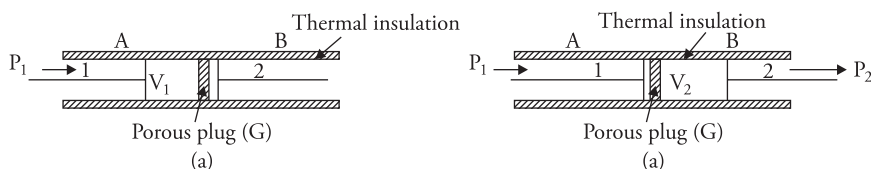


Figure 15.6 Throttled expansion of a gas

Let one mole of a gas occupy a volume V_1 between the piston 1 and plug G at constant pressure P_1 (Fig. 15.6(a)). When the piston is pressed forward, the gas flows across the ‘throttle’ consisting of a porous plug of silk or cotton. The gas coming out of the throttle (G) will push the piston 2 outwards. By the use of throttle, the expansion takes place slowly and the pressure on each side of the plug was maintained constant. The pressure on the left hand side is kept constant at a value of P_1 , whereas that on the right hand side is also kept constant but at a lower value P_2 .

The tube is made up of thermal insulation material and conditions are made adiabatic as far as possible, that is, no heat transfer takes place between system and surroundings. Now,

The external work done on the gas by piston 1 = $+P_1 V_1$

The external work done by the gas on piston 2 = $-P_2 V_2$

$$\therefore \text{the net work done by the gas} \quad w_1 = P_1 V_1 - P_2 V_2 \quad (1)$$

However, the process is carried out in an insulated chamber (adiabatically), that is, $q = 0$. Therefore, there is no exchange of heat between the system and the surroundings. This means that the work is done at the cost of the internal energy. The internal energy changes from E_1 to E_2 :

$$\Delta E = E_2 - E_1 \quad (2)$$

where E_1 denotes the internal energy in the initial state and E_2 is the internal energy of the final state.

The decrease in internal energy must be equal to the net work done w_1 by the system; hence, from Eqs. (1) and (2), we get

$$E_2 - E_1 = P_1 V_1 - P_2 V_2$$

$$\text{or} \quad E_1 + P_1 V_1 = E_2 + P_2 V_2$$

$$\text{or} \quad H_1 = H_2 \quad (\because H = E + PV)$$

$$\text{or } H_1 - H_2 = 0 \text{ or } \Delta H = 0.$$

Hence, it follows that the Joule–Thomson process (throttled expansion) is an isoenthalpic (constant enthalpy) process.

The Joule–Thomson Coefficient ($\mu_{J,T}$)

The heat content of a system, H , is an exact differential and is a function of two of the three variables P , V and T . If P and T are taken as independent variables, then

$$H = f(P, T)$$

On partial differentiation,

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT \quad (1)$$

As Joule–Thomson effect is an isoenthalpic process, $dH = 0$ and a subscript H is inserted to indicate the constant heat content. Eq. (1) changes to

$$0 = \left(\frac{\partial H}{\partial P} \right)_T dP_H + \left(\frac{\partial H}{\partial T} \right)_P dT_H$$

or,
$$\left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial H}{\partial P} \right)_T / \left(\frac{\partial H}{\partial T} \right)_P \quad (3)$$

$\left(\frac{\partial T}{\partial P} \right)_H$ is termed as the Joule–Thomson coefficient and is represented by the symbol $\mu_{J,T}$. It is defined as the rate of change of temperature with pressure in a streaming process through a plug or throttle.

$$\therefore \left(\frac{\partial H}{\partial T} \right)_P = C_P \quad (4)$$

Putting Eq. (4) in (3), we have

$$\mu_{J,T} = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T \quad (5)$$

since $H = E + PV$, Eq. (5) can also be written as

$$\mu_{J,T} = - \frac{1}{C_P} \left[\left(\frac{\partial E}{\partial P} \right)_T + \left(\frac{\partial(PV)}{\partial P} \right)_T \right] \quad (6)$$

As E is a function of P , V and T , which are not independent, Eq. (6) may be expressed as

$$\mu_{J,T} = -\frac{1}{C_p} \left[\left(\frac{\partial E}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial(PV)}{\partial P} \right)_T \right] \quad (7)$$

Concept of inversion temperature

For an ideal gas, $\left(\frac{\partial E}{\partial V} \right)_T$ is zero, and as $PV = RT$, $\left(\frac{\partial(PV)}{\partial P} \right)_T$ is also zero; hence, as C_p is finite, from Eq. (7) for an ideal gas $\mu_{JT} = 0$, hence the Joule–Thomson coefficient for an ideal gas should be zero which means that the temperature of an ideal gas does not change when it expands through a throttle.

However, unlike an ideal gas, the energy content of a real gas is not independent of volume. It has been shown that for real gas $\left(\frac{\partial E}{\partial V} \right)_T$ is usually positive. The factor, $\left(\frac{\partial V}{\partial P} \right)_T$ on the other hand, is always negative as at constant temperature increase in pressure is always accompanied by decrease in volume. Hence, the first term of Eq. (7) is usually negative.

Now turning to the second term $\left(\frac{\partial(PV)}{\partial P} \right)_T$ it is found that at low and moderate pressures, it is negative for all gases except hydrogen and helium (refer section 9.14). Thus, at low and moderate pressure, both the terms of the bracket are negative, and as heat capacity C_p is always positive, it follows that the Joule–Thomson coefficient μ_{JT} will have a positive value, which means that most gases experience a fall in temperature as a result of Joule–Thomson (throttled) expansion.

At high pressures, the first term remains constant but the second term decreases numerically and eventually becomes positive. Therefore, at sufficiently high pressure, there is a reversal of the Joule–Thomson effect, the coefficient μ_{JT} becomes negative. Under these conditions, a throttled expansion will be accompanied by an increase in temperature.

Hence, as the pressure increases the value of μ_{JT} changes from a positive value to a negative value. The temperature at which the Joule–Thomson effect changes sign, at a given pressure, is called the **inversion temperature**. At this temperature, the value of μ_{JT} is zero.

Hence, inversion temperature can be defined as that temperature at which the value of Joule–Thomson coefficient (μ_{JT}) is zero.

15.13 Limitations of the First Law: Need for the Second Law

The main limitations of the first law of thermodynamics are as follows:

- It simply establishes equivalence between different forms of energy. It does not describe the extent and conditions required to bring about the interconversion of energy from one form to the other. This can be understood by the following examples

It gives no information about the direction of flow of heat. If heat is flowing from a hot body to a cold body, the first law simply states that the heat lost is equal to the heat gained; it does not reveal that heat can flow only from the hot body to the cold body and not *vice versa*.

- (b) It gives no information regarding the feasibility of the process. For example, it does not indicate whether water can run uphill all by itself.
- (c) The first law states that when heat is converted into work, the work obtained is equivalent to the heat absorbed; however, it gives no information concerning the conditions under which the conversion is possible.
- (d) The first law of thermodynamics is a qualitative statement that fails to preclude the existence of either heat engines or a refrigerator. The first law fails to contradict the existence of a 100% efficient heat engine or a self-acting refrigerator. Practically, both the situations are unattainable.
- (e) It does not explain why most of the reactions do not proceed to completion. Consider the example of $\text{CO (g)} + \text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2\text{ (g)} + \text{H}_2\text{ (g)}$. If 1 mole of CO and 1 mole of H_2O is taken, then 1 mole of CO_2 and 1 mole of H_2 should be formed; however, the actual yield observed is less than 100%.

Spontaneous processes A process that can take place by itself without any external assistance is said to be a spontaneous process. The spontaneous processes are called feasible or probable processes. A spontaneous process takes place in one direction by itself, the reverse change can occur only when outside effort is provided. Spontaneous processes are irreversible. Some examples of spontaneous processes are as follows:

- (i) When a bar magnet is heated at one end then the heat conducts itself spontaneously from the hot end to the cold end until the temperature becomes uniform. This process cannot reverse itself spontaneously.
- (ii) The expansion of a gas into an evacuated space or from a region of high pressure to low pressure occurs spontaneously until the pressure becomes equal throughout. The reverse is not spontaneous.
- (iii) Diffusion of solute from concentrated to dilute occurs spontaneously without external intervention.

Reversible and spontaneous process

A reversible process is one that can proceed in either direction with equal ease. On the other hand, a spontaneous process is unidirectional and irreversible.

Non-spontaneous process

A non-spontaneous process is one that does not occur by itself. The process occurs by the application of external energy. For example, water can be lifted against gravity by pumping, that is, by application of an external force.

15.14 Statements of the Second Law of Thermodynamics

The various statements of the second law of thermodynamics are as follows:

- (a) *Kelvin–Planck statement* It is impossible to convert heat into work completely by a cyclic process without producing changes in some parts of the system.
- (b) *Clasius statement* For a self-acting machine, it is impossible to transfer heat from a body at a lower temperature to a body at a higher temperature without any external assistance or without at the same time converting some work into heat.

- (c) **Thomson statement** A continuous supply of work cannot be obtained by cooling a body to a temperature lower than that of its surroundings.

Although there are various statements for the second law of thermodynamics, the fundamental idea is that 'all forms of energy are convertible into heat but the heat so obtained cannot be converted into different forms of energy by any process'.

Carnot's heat engine

Any form of energy can perform work only when there is a difference of potential. Falling water does work because there is a potential energy difference at the two levels. Similarly, electrical work is done when there is electrical potential or electromotive force (EMF). In a heat reservoir at constant temperature there is no potential or driving force, hence no work can be done. However, two such reservoirs at different temperature provide a difference of energy potential that is necessary for the conversion of heat into work. This is in accordance with the second law of thermodynamics, which states that it is not possible to draw heat from a single source and convert it completely into work continuously. There must be at least two heat reservoirs at different temperatures to convert heat into mechanical work. This concept was utilized by S. Carnot (1824) in developing an ideal engine called Carnot engine to demonstrate the maximum convertibility of heat into work. The principle enunciated by Carnot was derived from the second law of thermodynamics and may be stated as '*all reversible heat engines operating between two given temperatures have the same efficiency*'. This means that if a machine functions in a thermodynamically reversible manner, the efficiency is independent of the working substance or mode of operation and depends only on the temperature of the source and sink.

Carnot's cycle It consists of four stages and is represented on a pressure–volume diagram. It demonstrates the maximum conversion of heat into work because the various steps are reversible and reversible work is the maximum possible work that a system can do.

Carnot's heat engine consists of an ideal machine containing 1 g mole of an ideal gas, which absorbs heat from its surroundings and converts it into work. The ideal machine is a cylinder fitted with a weightless and frictionless piston. The cylinder is perfectly insulated from all sides except the base, which can be brought in contact with thermostat at the required temperature or with insulator to prevent the flow of any heat inside or outside.

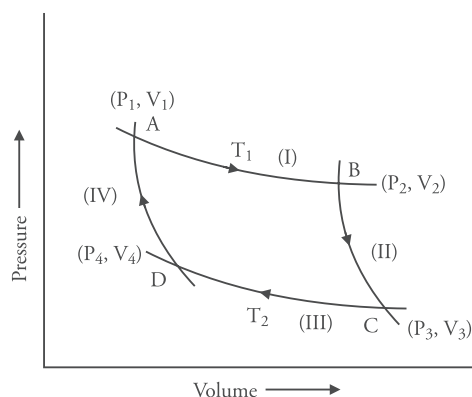


Figure 15.7 Pressure–volume changes in Carnot's cycle

The various stages of the Carnots cycle are as follows:

Step I Isothermal expansion The cylinder containing 1 mole of gas, occupying volume V_1 , is placed in contact with the source at temperature T_1 . The piston is allowed to move outwards infinitesimally slowly so that the gas expands isothermally and reversibly from volume V_1 (at A) to volume V_2 (at B). The curve AB represents the isothermal expansion of the ideal gas at constant temperature.

As in this change, the temperature is maintained constant (i.e., $\Delta E = 0$), the heat absorbed q_1 will be used only in doing the work w_1 by the system on its surroundings, that is,

$$q_1 = -w_1 = RT_1 \ln \frac{V_2}{V_1} \quad (1)$$

Step II Adiabatic expansion The cylinder of gas is removed from the reservoir at T_1 and is surrounded by a non-conducting jacket so that the gas expands reversibly and adiabatically from V_2 (at B) to V_3 (at C) and consequently the temperature falls from T_1 to T_2 . As the process is adiabatic ($\delta q = 0$), the amount of work done w_2 by the gas will be given as

$$\Delta E = -w_2 = -C_V(T_1 - T_2) = C_V(T_2 - T_1) \quad (2)$$

Step III Isothermal compression The non-conducting jacket is now removed and the cylinder is placed in the heat reservoir at T_2 . The volume of the gas decreases from V_3 (at C) to V_4 (at D). Heat produced in this process is rejected to the sink. If q_2 is the heat rejected to the surroundings at temperature T_2 and w_3 is the work done on the gas, then

$$q_2 = w_3 = RT_2 \ln \frac{V_4}{V_3} \quad (3)$$

Step IV Adiabatic compression The cylinder is removed from the heat reservoir and the non-conducting jacket is replaced. The gas is then compressed adiabatically till it acquires the temperature T_1 and volume V_1 at A. The work done on the gas is given by

$$w_4 = +\Delta E = C_V(T_1 - T_2) \quad (4)$$

where $T_1 - T_2$ is the increase in temperature produced by adiabatic compression.

The network done in the cyclic process is

$$\begin{aligned} w &= -w_1 + (-w_2) + w_3 + w_4 \\ w &= RT_1 \ln \frac{V_2}{V_1} - C_V(T_1 - T_2) + RT_2 \ln \frac{V_4}{V_3} + C_V(T_1 - T_2) \\ w &= RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_3}{V_4} \end{aligned} \quad (5)$$

Net heat absorbed

$$q = q_1 - q_2 = RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_3}{V_4}$$

Thus, we see that $w = q$ or the work done is maximum. Hence, the heat absorbed by the gas is equal to the work done by it, which is in accordance with the first law of thermodynamics.

Efficiency of heat engine

The efficiency of an engine is defined as the fraction of the heat absorbed by the engine that it can convert into work. Thus, for the above cycle, maximum efficiency is

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat drawn from the source}} = \frac{q_1 - q_2}{q_1}$$

$$= \frac{RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_3}{V_4}}{RT_1 \ln \frac{V_2}{V_1}} \quad (6)$$

$$= \frac{T_1 \ln \frac{V_2}{V_1} - T_2 \ln \frac{V_3}{V_4}}{T_1 \ln \frac{V_2}{V_1}} \quad (7)$$

As A and D lie on one adiabatic curve, whereas B and C on another adiabatic curve, we have

$$\frac{T_1}{T_2} = \left(\frac{V_3}{V_2} \right)^{\gamma-1} \quad \text{and} \quad \frac{T_1}{T_2} = \left(\frac{V_4}{V_1} \right)^{\gamma-1}$$

Consequently,

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting this in Eq. (7) we get

$$\eta = \frac{T_1 \ln \frac{V_2}{V_1} - T_2 \ln \frac{V_2}{V_1}}{T_1 \ln \frac{V_2}{V_1}}$$

$$= \frac{(T_1 - T_2) \ln \frac{V_2}{V_1}}{T_1 \ln \frac{V_2}{V_1}}$$

$$= \frac{T_1 - T_2}{T_1} \quad (8)$$

Eq. (8) gives the efficiency of any reversible heat engine operating between the temperature T_1 and T_2 . From the equation it is evident that

- For an engine to have 100% efficiency, T_2 must be zero, that is, the temperature of the sink should be absolute zero.

- As absolute zero temperature cannot be realized in actual practice, a heat engine with 100% efficiency is not possible.

Hence ‘the efficiency (η) of a heat engine is always less than unity.’

Solved examples

1. A Carnot's cycle working between 0 °C and 100 °C takes up 840 Joule from the high-temperature reservoir. Calculate the work done, the heat rejected and efficiency.

Solution

$$T_1 = 273 + 100 = 373 \text{ K}; T_2 = 273 + 0 = 273 \text{ K}; q_1 = 840 \text{ J}; q_2 = ?$$

$$\text{we know } \eta = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\text{or } \frac{q_2}{q_1} = \frac{T_2}{T_1}$$

$$\text{or } q_2 = \frac{T_2}{T_1} \times q_1 = \frac{273 \times 840}{373} = 614.79 \text{ J}$$

$$\therefore \text{work done, } w = q_1 - q_2 = 840 - 614.79 = 225.21 \text{ J}$$

$$\text{Heat rejected} = q_2 = 614.79 \text{ J.}$$

$$\text{Efficiency } \eta = \frac{T_1 - T_2}{T_1} = \frac{373 - 273}{373} = 0.268 = 26.8\%$$

2. A Carnot's engine works between 120 °C and 30 °C. Calculate the efficiency. If the power produced by the engine is 400 watt, calculate the heat absorbed from the source and rejected to the sink every second.

Solution

$$\text{Efficiency } \eta = \frac{T_1 - T_2}{T_1}$$

$$T_1 = 273 + 120 = 393 \text{ K}; T_2 = 273 + 30 = 303 \text{ K}$$

$$\eta = \frac{393 - 303}{393} = 0.229 = 22.9\%$$

$$\text{again } \eta = \frac{q_1 - q_2}{q_1} = \frac{w}{q_1}$$

$$\therefore q_1 = \frac{w}{\eta} = \frac{400}{0.229} = 1747 \text{ watt}$$

$$\text{also } \frac{q_2}{q_1} = \frac{T_2}{T_1}$$

$$\therefore \text{the heat rejected to the sink}$$

$$q_2 = q_1 \times \frac{T_2}{T_1} = 1747 \times \frac{303}{393} = 1347 \text{ watt}$$

3. A Carnot's engine working between two temperatures has an efficiency of 40%. When the temperature of the sink is reduced by 60 °C, the efficiency increases to 55%. Calculate the two temperatures in the first case.

Solution

$$\text{Efficiency } \eta = 0.4 = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \quad (1)$$

$$\therefore \frac{T_2}{T_1} = 1 - 0.4 = 0.6$$

when the temperature of the sink is reduced by 60 °C we get efficiency

$$\eta = 0.55 = \frac{T_1 - (T_2 - 60)}{T_1} = 1 - \frac{(T_2 - 60)}{T_1} \quad (2)$$

$$\frac{(T_2 - 60)}{T_1} = 1 - 0.55 = 0.45$$

On dividing Eq. (2) by (1) we obtain

$$\frac{(T_2 - 60)}{T_2} = \frac{0.45}{0.60} = \frac{3}{4}$$

$$\text{or } 4T_2 - 240 = 3T_2$$

$$T_2 = 240 \text{ K}$$

Placing the value of T_2 in Eq. (1) we get

$$\frac{240}{T_1} = 0.6$$

$$T_1 = \frac{240}{0.6} = 400 \text{ K}$$

Practice problems

- The boiling point of water at 50 atm pressure is 265 °C. Compare the theoretical efficiency of the system of engine operating between 45 °C and the boiling point of water at (i) 1 atm and (ii) 50 atm. [Ans (i) 14.75% (ii) 40.89%]
- The efficiency of an engine is 0.42. Calculate the heat that must be withdrawn from the reservoir at higher temperature to produce 203 cal of work. [Ans 483.3 cal]
- What percent of T_2/T_1 gives heat engine an ideal efficiency of 10%? [Ans $T_2/T_1 = 0.9$]

15.15 Entropy

The original statement of the second law of thermodynamics is concerned with the development of the theoretical aspect of heat engine, specially the Carnot's cycles. This has little implication in the chemical processes.

For a chemist, attempts were made to answer the question of feasibility of a reaction. As is known that a state with minimum energy is the most stable state of a system, therefore, in this universe there is a natural tendency of all systems to stabilise by acquiring minimum energy. It was believed that all processes in which energy decreases (exothermic, having negative value of ΔH) occur spontaneously. Hence, decrease in enthalpy is the driving force behind the spontaneous processes. However, there are many endothermic reactions (ΔH positive) that are spontaneous. For example,

- Water absorbs energy and is evaporated (endothermic process) but it is spontaneous in nature.

$$\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)} \quad \Delta H = + 44.0 \text{ kJ mol}^{-1}$$
- Melting of ice is endothermic but spontaneous.
- A crystal of potassium permanganate dropped in a beaker spontaneously diffuses in water without any perceptible change in the heat content.
- Salts like ammonium nitrate dissolve spontaneously by absorption of heat.

How are these processes spontaneous? It is definite that this cannot be explained by considering the decrease in enthalpy alone. There are some additional contributory factors to the spontaneity of these reactions; it is this search for another factor that has resulted in describing another property of the system called **entropy**.

Entropy and its physical significance

To explain this term let us consider a process that does not involve energy changes or is endothermic.

Mixing of two gases Let us consider a box having two partitions, each having a different gas. When this partition is lifted, the diffusion of gases occurs and they get mixed up. We can also say that the gas molecules now have a larger space for their movement. In statistical language, we can say that the probability of finding a molecule at a particular place or point has decreased or the chaos has increased.

Conversion of solids into liquids When a solid melts into a liquid ($\Delta H = +ve$), the particles have more freedom to move in the liquid state. Similarly, ammonium nitrate dissolves in water, the solid particles leave their lattice position and move about freely in the dissolved state. Hence, we can say that the randomness or disorder increases.

Entropy is a property that is used to express this extent of disorder or randomness of a system and may be defined as the thermodynamic property that is a measure of the randomness or disorder of the molecules of a system.

Mathematical formulation of entropy

The concept of entropy was first introduced in connection with the theory of heat engines and it is more important for engineers. It was only later that chemists could make use of it in chemical processes.

Entropy is expressed by the symbol 'S'. Like internal energy and enthalpy, entropy is also a state function and therefore change in entropy depends only on the initial and final states of the system.

Change in entropy is given by

$$\Delta S = S(\text{final state}) - S(\text{initial state}).$$

For a reversible process at equilibrium, the change in entropy is expressed as

$$dS = \frac{dq_{\text{rev}}}{T}$$

Thus, entropy change may be defined as the amount of heat absorbed by the system in a reversible manner divided by the absolute temperature at which the heat is absorbed.

Units of entropy

As entropy change is expressed as heat divided by temperature, the units of entropy are calories per degree (expressed as entropy unit eu, 1 eu = 1 cal deg⁻¹) or Joule per Kelvin (J K⁻¹). (For 1 mole of a substance the units of entropy are cal deg⁻¹mol⁻¹. This is called molar entropy)

15.16 Second Law of Thermodynamics in Terms of Entropy

If gases are mixed in an isolated system, then there is no exchange of energy or matter between the system and the surroundings. The process occurs because the randomness or entropy increases. Hence, for a spontaneous process in an isolated system, entropy change is positive, that is, $\Delta S > 0$. However, if the system is not isolated, the entropy changes of both the system and surroundings have to be taken into account. Then, the sum of entropy changes of the system (ΔS_{system}) and the surrounding ($\Delta S_{\text{surroundings}}$) gives the total entropy change (ΔS_{total}).

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

For a spontaneous process, ΔS_{total} must be positive, that is,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0.$$

The system and the surroundings together constitute the universe. Therefore, for a spontaneous change,

$$\Delta S_{\text{universe}} > 0.$$

Hence, according to the second law of thermodynamics '*in any natural process the energy of the universe is conserved but the entropy of the universe always increases*'.

Entropy is a state function

In the definition of entropy, the quantity q_{rev} is not a state function and depends on the path of the reaction, whereas the $\frac{dq_{\text{rev}}}{T}$ is a perfect differential. This can be shown as follows:

Suppose 1 mole of an ideal gas is undergoing a reversible expansion. From the first law,

$$dq_{\text{rev}} = dE - dw$$

For work expansion $-dw = PdV$ hence,

$$\begin{aligned} dq_{\text{rev}} &= dE + PdV \quad (1) & (\because PV = RT, \quad P = \frac{RT}{V} \quad \text{similarly} \quad C_v = \left(\frac{\partial E}{\partial T} \right)_v \\ & & \text{or } dE = C_v dT) \\ &= C_v dT + \frac{RT}{V} dV \\ \text{or } dq_{\text{rev}} &= \int C_v dT + \int \frac{RT}{V} dV \end{aligned} \quad (2)$$

As dq_{rev} is not an exact differential, it cannot be integrated. This is confirmed by observing the right hand side of Eq. (2) where $\int \frac{RT}{V} dV$ cannot be evaluated unless we specify the path or in other words the relation between T and V is known. The value of V will be different for different values of T . Thus, dq_{rev} depends on the path by which the gas is expanded. Dividing Eq. (2) by T on both sides we get

$$\begin{aligned} \int \frac{dq_{\text{rev}}}{T} &= \int \frac{C_v dT}{T} + \int \frac{RT}{V} \frac{1}{T} dV \\ &= \int \frac{C_v dT}{T} + \int \frac{R}{V} dV \\ &= C_v \ln T + R \ln V + \text{constant} \end{aligned}$$

It follows that $\int \frac{dq_{\text{rev}}}{T}$ can be evaluated; hence, $\frac{dq_{\text{rev}}}{T}$ is an exact differential. Hence, we may conclude that entropy change dS is a perfect differential and hence entropy S is a state function.

Thus, if a system changes from the initial state 1 to the final state 2, the entropy change is expressed by integrating the equation $S = \frac{dq_{\text{rev}}}{T}$ between the limits of the initial state 1 and final state 2.

$$\begin{aligned} \int_1^2 dS &= \int_1^2 \frac{dq_{\text{rev}}}{T} \\ \Delta S &= S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} \end{aligned}$$

where S_1 and S_2 are the entropies of the system in initial and final states respectively.

It must be born in mind that entropy change dS is equal to the amount of heat absorbed divided by the absolute temperature only when the process is carried out reversibly.

15.17 Evaluation of Entropy

1. Entropy changes for an ideal gas

Consider a system consisting of n moles of an ideal gas occupying a volume V at a pressure P and temperature T . If dq_{rev} amount of heat is absorbed by the system reversibly, then the increase in entropy of the system dS is given by

$$dS = \frac{dq_{\text{rev}}}{T} \quad (1)$$

From the first law of thermodynamics, for a reversible process in which only pressure – volume work is involved

$$dq_{\text{rev}} = dE - dw$$

For work expansion there is infinitesimal increase in volume dV against pressure P , hence $-dw = PdV$

$$\therefore dq_{\text{rev}} = dE + PdV \quad (2)$$

Substituting the value of dq_{rev} in Eq. (1) we get

$$dS = \frac{dE + PdV}{T} \quad (3)$$

For n moles of an ideal gas, we know that

$$PV = nRT \quad \text{and} \quad dE = nC_V dT$$

where C_V is the molar heat at constant volume.

Substituting these values in Eq. (3) we get,

$$dS = \frac{nC_V dT + \frac{nRT}{V} dV}{T}$$

or
$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} \frac{nC_V dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V} \quad (4)$$

If the entropy, volume and temperature of the system in the initial state are S_1, V_1 and T_1 and in the final state are S_2, V_2 and T_2 respectively, then integrating Eq. (4) between these limits we get

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_V \frac{dT}{T} + \int_{V_1}^{V_2} nR \frac{dV}{V}$$

Assuming C_V to be independent of temperature over the temperature range considered, we obtain

$$\Delta S = S_2 - S_1 = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \dots\dots\dots(5)$$

For 1 mole of an ideal gas,

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{.....(6)} \quad (6)$$

An alternate form of Eq. (5) involving pressure terms can be obtained in the following manner

If P_1 is the pressure of the system in the initial state and P_2 in the final state, then from the gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or
$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1}$$

Substituting in Eq. (5) we obtain,

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1 T_2}{P_2 T_1}$$

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= n(C_V + R) \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

Since $(C_V + R) = C_P$ Hence

$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \quad (7)$$

From Eqs (5), (6) and (7), entropy change for an ideal gas can be calculated. These equations take different forms under different conditions.

(i) **For isothermal process** When $T_1 = T_2$ then Eqs (5) and (7) are reduced to

$$\Delta S_T = nR \ln \frac{V_2}{V_1} \quad \text{.....(8)} \quad (8)$$

and
$$\Delta S_T = nR \ln \frac{P_1}{P_2} \quad \text{.....(9)} \quad (9)$$

The subscript T in ΔS_T indicates that the process is occurring at constant temperature. In the expansion process $V_2 > V_1$ or $P_1 > P_2$, ΔS_T is positive but in contraction $V_2 < V_1$ or $P_1 < P_2$ and hence ΔS_T is negative. From this, it is concluded that in an isothermal expansion entropy increases and in contraction it decreases.

(ii) **For an isobaric process** When $P_1 = P_2$, Eq. (7) reduces to

$$\Delta S_P = nC_P \ln \frac{T_2}{T_1} \quad (10)$$

- (iii)
- For an isochoric process**
- When
- $V_1 = V_2$
- , then Eq. (6) reduces to

$$\Delta S_V = nC_V \ln \frac{T_2}{T_1} \quad (11)$$

Solved examples

1. Calculate the change in entropy accompanying the isothermal expansion of 5 moles of an ideal gas at 330 K until its volume has increased six times.

Solution

Entropy change during isothermal expansion of an ideal gas

$$\begin{aligned} (\Delta S)_T &= 2.303nR \log \frac{V_2}{V_1} = 2.303 \times 5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \log \frac{6}{1} \\ &= 2.303 \times 5 \times 8.314 \times 0.7782 = 74.5 \text{ J K}^{-1} \end{aligned}$$

2. Calculate the entropy change involved in expanding 1 mole of an ideal gas from 15 L at 2 atm pressure to 50 L at 1 atm pressure. ($C_p = 7.42 \text{ cal deg}^{-1} \text{ mol}^{-1}$)

Solution

$$\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 2.303nC_p \log_{10} \frac{T_2}{T_1} + 2.303 nR \log_{10} \frac{P_1}{P_2}$$

$$n = 1 \text{ mole}; \quad C_p = 7.42 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}; \quad P_1 = 2 \text{ atm}; \quad P_2 = 1 \text{ atm}$$

$$\text{For an ideal gas } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{or } \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \frac{50 \times 1}{15 \times 2} = \frac{5}{3}$$

$$\therefore \Delta S = 2.303 \times 1 \times 7.4 \log_{10} \frac{5}{3} + 2.303 \times 1 \times 1.987 \log_{10} \frac{2}{1}$$

$$= 3.779 + 1.377 = 5.156 \text{ cal deg}^{-1}$$

3. Calculate the entropy change when 3 moles of an ideal gas ($C_v = 7.88 \text{ cal deg}^{-1} \text{ mol}^{-1}$) are heated from a volume of 200 L at 50 °C to a volume of 300 L at 150 °C.

Solution

$$\Delta S = 2.303 nC_v \log_{10} \frac{T_2}{T_1} + 2.303 nR \log_{10} \frac{V_2}{V_1}$$

Here, $n = 3$ mole, $C_V = 7.88 \text{ cal deg}^{-1} \text{ mol}^{-1}$ $R = 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$

$T_1 = 273 + 50 = 323 \text{ K}$; $T_2 = 273 + 150 = 423 \text{ K}$; $V_1 = 200 \text{ L}$; $V_2 = 300 \text{ L}$.

$$\begin{aligned}\Delta S &= 2.303 \times 3 \times 7.88 \log_{10} \frac{423}{323} + 2.303 \times 3 \times 1.987 \times \log_{10} \frac{300}{200} \\ &= 6.377 + 2.417 = 8.794 \text{ cal deg}^{-1}\end{aligned}$$

4. Calculate the entropy change when 1 mole of an ideal gas is heated from 20°C to 40°C at a constant pressure. The molar heat at constant pressure of the gas over this temperature range is $6.189 \text{ cal deg}^{-1}$.

Solution

For an isobaric process,

$$\Delta S_p = 2.303 n C_p \log_{10} \frac{T_2}{T_1}$$

Here

$n = 1 \text{ mole}$; $C_p = 6.189 \text{ cal deg}^{-1}$

$T_1 = 273 + 20 = 293 \text{ K}$; $T_2 = 273 + 40 = 313 \text{ K}$

$$\begin{aligned}\Delta S_p &= 2.303 \times 1 \times 6.189 \times \log_{10} \frac{313}{293} \\ &= 0.4087 \text{ cal deg}^{-1}\end{aligned}$$

Practice problems

- 1 mole of an ideal gas ($C_V = 12.55 \text{ J K}^{-1} \text{ mol}^{-1}$) is transferred from 298 K and 2 atm to 233 K and 0.4 atm . Calculate the value of entropy change in the system.
[Ans $10.294 \text{ J K}^{-1} \text{ mol}^{-1}$]
- 1 mole of an ideal gas ($C_V = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$) is heated from 300 to 600 K . Calculate entropy change when (a) volume is kept constant, (b) pressure is kept constant.
[Ans (a) $8.645 \text{ J K}^{-1} \text{ mol}^{-1}$ (b) $14.408 \text{ J K}^{-1} \text{ mol}^{-1}$]
- Calculate the entropy change when 5 moles of an ideal gas undergoes isothermal expansion at 20°C from a pressure of 10 atm to a pressure of 2 atm .
[Ans $66.909 \text{ J deg}^{-1}$]
- Calculate the entropy change when 2 mole of an ideal gas is allowed to expand from a volume of 1 L to a volume of 10 L at 27°C .
[Ans 38.294 J K^{-1}]

2. Entropy change in heating a solid or a liquid

When a solid or a liquid is heated without producing change in state, the heat change is given by

Quantity of heat absorbed = mass \times specific heat \times temperature rise.

= number of moles \times molar heat \times temperature rise.

Thus, if $m \text{ g}$ of a solid or a liquid of specific heat s is heated reversibly through temperature dT , the amount of heat absorbed is given by

$$dq_{\text{rev}} = msdT$$

$$\therefore \text{Entropy change} \quad dS = \frac{dq_{\text{rev}}}{T} = \frac{msdT}{T}$$

$$\text{or} \quad \int \Delta S = \int_{T_1}^{T_2} \frac{msdT}{T} \quad (12)$$

Assuming that s remains constant within the temperature limits T_1 and T_2 , Eq. (12) on integration gives,

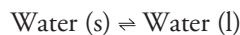
$$\Delta S = ms \ln \frac{T_2}{T_1} = 2.303 \, ms \log_{10} \frac{T_2}{T_1} \quad (13)$$

3. **Entropy change during phase transition** When matter changes from one phase to another like from the solid phase to the liquid phase or from liquid to gaseous phase, then it is termed as the phase transition. Melting of solid or vaporisation of liquid occurs at constant temperature as the two phases are in equilibrium at all times. The entropy change for these reactions may be calculated as

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where q is the heat evolved or absorbed during transition and T is the temperature. For transformation of 1 mole of a substance at constant pressure, q_{rev} is equal to the molar enthalpy change for that transformation, that is, $q_{\text{rev}} = \Delta H_{\text{trans}}$. Let us consider some examples

- (i) **Entropy of fusion** Entropy of fusion is the entropy change during the conversion of 1 mole of the solid substance into liquid form at its melting point. For example, when ice melts,



The change in entropy is given by

$$S_{\text{water}} - S_{\text{ice}} = \Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad (14)$$

where ΔH_{fusion} the enthalpy of fusion and T_f is the fusion temperature.

- (ii) **Entropy of vaporisation** Entropy of vaporisation is the change in entropy when 1 mole of a liquid changes into vapor at its boiling point. The entropy of vaporisation of a liquid at its boiling point is

$$\Delta S_{\text{vaporization}} = \frac{\Delta H_{\text{vap}}}{T_b} \quad (15)$$

where ΔH_{vap} is the entropy of vaporisation and T_b is the boiling point.

Practice problems

1. Calculate the entropy change when 2 moles of lead is heated from 27 °C to 28 °C. The specific heat of lead over this temperature range is 0.03 cal g⁻¹ and the atomic weight of lead is 207.

Solution

$$\Delta S = 2.303 \, m s \log_{10} \frac{T_2}{T_1}$$

Here, $m = 2 \times 207 = 414 \text{ g}$; $s = 0.03 \text{ cal g}^{-1}$; $T_1 = 273 + 27 = 300 \text{ K}$; $T_2 = 273 + 28 = 301 \text{ K}$.

$$\begin{aligned} \Delta S &= 2.303 \times 414 \times 0.03 \times \log_{10} \frac{301}{300} \\ &= 0.0413 \text{ cal K}^{-1} \end{aligned}$$

2. Calculate the molar entropy of vaporisation of 1 mole of water at 100 °C. Latent heat of vaporisation of water at 100 °C is 540 cal/g.

Solution

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{540 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{373} = 26.059 \text{ cal mol}^{-1} \text{ K}^{-1}$$

3. Calculate the total entropy change when 5 moles of ice at 0 °C and 1 atm is converted into steam at 100 °C. The molar heat of fusion of ice and molar heat of vaporisation of water are 1440 and 9720 cal mol⁻¹. The molar heat capacity of water over this temperature range may be taken equal to 18 cal mol⁻¹.

Solution

The process is irreversible. To compute the entropy change, the given process may be imagined to be carried out reversibly in the following three steps

- (i) $\text{H}_2\text{O (s) at } 0^\circ\text{C} \rightarrow \text{H}_2\text{O (l) at } 0^\circ\text{C}$.
- (ii) $\text{H}_2\text{O (l) at } 0^\circ\text{C} \rightarrow \text{H}_2\text{O (l) at } 100^\circ\text{C}$.
- (iii) $\text{H}_2\text{O (l) at } 100^\circ\text{C} \rightarrow \text{H}_2\text{O (g) at } 100^\circ\text{C}$.

The molar entropy change for process (i) is given by

$$\Delta S_1 = \frac{\Delta H_{\text{fusion}}}{T_f} = \frac{1440}{273} = 5.274 \text{ cal mol}^{-1} \text{ K}^{-1}$$

The molar entropy change in process (ii) is given by

$$\begin{aligned} \Delta S_2 &= 2.303 C_p \log_{10} \frac{T_2}{T_1} \\ &= 2.303 \times 18 \times \log_{10} \frac{373}{273} = 5.616 \text{ cal mol}^{-1} \text{ K}^{-1} \end{aligned}$$

The molar entropy change in process (iii) is given by

$$\Delta S_3 = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{9720}{373} = 26.06 \text{ cal mol}^{-1} \text{ K}^{-1}$$

∴ The total molar entropy change $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

$$= 5.274 + 5.616 + 26.06 = 36.95 \text{ cal K}^{-1} \text{ mol}^{-1}.$$

The total entropy change for 5 moles = $5 \times 36.95 = 184.75 \text{ cal K}^{-1}$.

4. ΔS_{vap} of acetone is $93.0 \text{ J K}^{-1} \text{ mol}^{-1}$. If the boiling point of acetone is 56°C , calculate the heat required to vaporise 1 g of acetone.

Solution

$$\Delta S_{\text{vap}} = 93.0 \text{ J K}^{-1} \text{ mol}^{-1} ; T_b = 273 + 56 = 329 \text{ K}.$$

$$\Delta S_{\text{vap}} = \frac{\Delta H}{T_b}$$

$$\Delta H = \Delta S_{\text{vap}} \times T_b = 93 \times 329 = 30597 \text{ J mol}^{-1}$$

$$\text{Heat required to vaporise 1 mole acetone} = 58 \text{ g} = 30597 \text{ J mol}^{-1}$$

$$\therefore \text{Heat required to vaporise 1 g acetone} = \frac{30597}{58} = 527.5 \text{ J}$$

Practice problems

- Determine the entropy of fusion of ice, if its latent heat of fusion is $6.025 \text{ kJ mol}^{-1}$.
[Ans = $22.07 \text{ J K}^{-1} \text{ mol}^{-1}$]
- Find the change in entropy when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is $9522 \text{ cal mol}^{-1}$.
[Ans = $27.128 \text{ cal K}^{-1} \text{ mol}^{-1}$]
- 30.4 kJ of heat is required to melt 1 mole of sodium chloride. The entropy change during melting is $28.4 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the melting point of sodium chloride.
[Ans = 1070.4 K]
- If $\Delta S = 109.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and boiling point of ethanol = 78.5°C , find out the enthalpy of vaporisation per mole for ethanol
[Ans $38.595 \text{ kJ mol}^{-1}$]

15.18 Entropy Changes in a Reversible Process

Total entropy change of the universe can be evaluated by considering the entropy change of the system as well as that of the surroundings. When a system gains heat, the surrounding loses heat and hence their entropies also change. The total change in entropy will, therefore, be equal to the algebraic sum of the entropy change of the system and the surroundings, that is,

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

If an ideal gas undergoes an isothermal reversible expansion and absorbs heat equal to q_{rev} at temperature T , then the entropy change of the gas, that is, system is given by

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T}$$

As the expansion is reversible, the system is in equilibrium with its surroundings at all times during the expansion. Hence, the surroundings lose an amount of heat equal to q_{rev} or we can say that the surrounding absorb $(-)$ q_{rev} of heat. The entropy change of the surroundings is given by

$$\Delta S_{\text{surroundings}} = -\frac{q_{\text{rev}}}{T}$$

\therefore the total entropy change of the universe,

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T}$$

$$\Delta S = 0 \quad (16)$$

Hence, it can be concluded that for a reversible process the total entropy change of the universe is zero.

However a thermodynamically irreversible process is always accompanied by an increase in entropy of the system and surroundings taken together .

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

15.19 Entropy Change in a Irreversible Process

In an irreversible or spontaneous process, the entropy of the universe increases. This can be illustrated by taking the following examples

- (i) **Isothermal expansion of an ideal gas** Consider an irreversible isothermal expansion of an ideal gas. Suppose n moles of an ideal gas expands irreversibly from a volume V_1 to a volume V_2 , as ΔS_{system} is independent of the path of the change it is given by

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

The entropy change of the surroundings will, however, be different. Let us take the extreme case of isothermal free expansion, that is, expansion in vacuum. In this case no work is done by the gas, that is, $w = 0$. For an isothermal process, $\Delta E = 0$. According to the first law of thermodynamics,

$$q = \Delta E - w.$$

$$= 0 + 0 = 0.$$

This shows that no heat is absorbed by the system and as such no heat will be given up by the surroundings and consequently

$$\Delta S_{\text{surroundings}} = 0$$

∴ the total entropy change of the universe-

$$\Delta S = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= nR \ln \frac{V_2}{V_1} + 0$$

$$\text{or } \Delta S = nR \ln \frac{V_2}{V_1}$$

As $V_2 > V_1$, the value of ΔS is positive; hence, in an irreversible expansion of an ideal gas the entropy of the universe increases.

German physicist Rudolf Clausius (1822–1888) summed up the first and second law stating that: the energy of the universe remains constant and the entropy of the universe tends towards a maximum.

15.20 Entropy of Mixing

When different gases are allowed to mix freely at constant temperature and pressure, there is an increase in entropy. On mixing, the molecules of each gas are free to move in a large volume, that is, their randomness increases and hence entropy increases.

Quantitative expression

Entropy change (dS) for 1 mole of an ideal gas is given by

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V}$$

Assuming C_v to be constant for an ideal gas and integrating this equation, we get

$$\int dS = C_v \int \frac{dT}{T} + R \int \frac{dV}{V}$$

$$S = C_v \ln T + R \ln V + S_0 \quad \{S_0 = \text{integration constant}\} \quad (17)$$

$$\text{Now } V = \frac{RT}{P}$$

Placing the value of V in Eq. (17), we have

$$S = C_v \ln T + R \ln T + R \ln R - R \ln P + S_0$$

$$S = C_p \ln T - R \ln P + S'_0 \quad (\because C_p = C_v + R)$$

$$\text{where } S'_0 = R \ln R + S_0$$

Now, let us consider a gaseous mixture containing n_1, n_2, \dots , etc., moles of various gases and let their partial pressures be p_1, p_2, \dots , etc., respectively, then entropy of the mixture is

$$S = n_1(C_p \ln T - R \ln p_1 + S'_0) + n_2(C_p \ln T - R \ln p_2 + S'_0) + \dots$$

$$= \sum n(C_p \ln T - R \ln p + S'_0)$$

Now partial pressure (p) = Mole fraction(X) \times Total pressure P

$$\therefore S = \sum n(C_p \ln T - R \ln P + R \ln X + S'_0)$$

Entropy change during mixing of ideal gases

Suppose n_1, n_2, \dots , etc., are the number of moles of ideal gas 1, 2, ... etc., and V_1, V_2, \dots etc., are the volumes of the individual gas. Then, at constant temperature

$$\Delta S_{\text{mixing}} = S_{\text{final}} - S_{\text{initial}}$$

$$= [n_1 R \ln(V_1 + V_2 + \dots) - n_1 R \ln V_1] - [n_2 R \ln(V_1 + V_2 + \dots) - n_2 R \ln V_2] + \dots$$

$$= -n_1 R \ln \frac{V_1}{(V_1 + V_2 + \dots)} - n_2 R \ln \frac{V_2}{(V_1 + V_2 + \dots)}$$

But $\frac{V_1}{(V_1 + V_2 + \dots)} = \frac{n_1}{n_i} = X_1$; $\frac{V_2}{(V_1 + V_2 + \dots)} = \frac{n_2}{n_i} = X_2$

where n_i is the total number of moles in the gases in the system and X gives the mole fraction of the individual gases.

$$\therefore \Delta S_{\text{mixing}} = -R[n_1 \ln X_1 + n_2 \ln X_2 \dots]$$

$$= -R \sum n_i \ln X_i$$

$$= -R \sum X_i \ln X_i \quad (\because X_i \propto n_i) \quad (18)$$

It is interesting to note that mole fraction X_i of any gas in a mixture must be less than unity, its logarithm is negative, hence ΔS_{mixing} as defined by Eq. (18) is always positive. Hence, the mixing of two or more gases is always accompanied by an increase in entropy.

Solved examples

1. Calculate the entropy of mixing of 1 mole of N_2 and 2 moles of O_2 , assuming the gases to be ideal. Express the result in S.I. units.

Solution

$$\Delta S_{\text{mix}} \text{ per mole} = -2.303R[n_1 \log X_1 + n_2 \log X_2]$$

$$X_1 = \frac{\text{moles of } N_2}{\text{Total number of moles}} = \frac{1}{3} ; X_2 = \frac{\text{moles of } O_2}{\text{Total number of moles}} = \frac{2}{3}$$

$$\begin{aligned}
\Delta S_{\text{mix}} &= -2.303 \times 8.314 \left[\frac{1}{3} \log \frac{1}{3} + \frac{2}{3} \log \frac{2}{3} \right] \text{ J K}^{-1} \\
&= +2.303 \times 8.314 \left[\frac{1}{3} \log 3 + \frac{2}{3} \log \frac{3}{2} \right] \text{ J K}^{-1} \\
&= 2.303 \times 8.314 (0.1590 + 0.1174) \text{ J K}^{-1} \\
&= 5.29 \text{ J K}^{-1} \\
\text{for 3 moles } \Delta S_{\text{mix}} &= 3 \times 5.29 = 15.87 \text{ J K}^{-1}
\end{aligned}$$

2. At NTP, 2.8 L of oxygen were mixed with 19.6 L of hydrogen. Calculate the increase in entropy, assuming ideal gas behavior.

Solution

Here,

$$n_1 = \frac{2.8 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.125 \text{ mol}; \quad n_2 = \frac{19.6 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.875 \text{ mol}$$

$$X_1 = \frac{0.125}{0.125 + 0.875} = 0.125 \quad \text{and} \quad X_2 = \frac{0.875}{0.125 + 0.875} = 0.875$$

$$\begin{aligned}
\Delta S_{\text{mixing}} &= -R \times 2.303 [n_1 \log X_1 + n_2 \log X_2] \\
&= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303 [0.125 \text{ mol log } 0.125 + 0.875 \text{ mol log } 0.875] \\
&= -8.314 \times 2.303 [-0.1129 - 0.0507] \\
&= 8.314 \times 2.303 \times (-0.1636) = 3.132 \text{ J K}^{-1}
\end{aligned}$$

3. The mixing of gases is always accompanied by an increase in entropy. Show that in the formation of a binary mixture of two ideal gases the maximum entropy increase results when $X_1 = X_2 = 0.5$

Solution

For a binary mixture the entropy per mole of the mixture formed is given by

$$\begin{aligned}
\Delta S_{\text{mixing}} &= -R [X_1 \ln X_1 + X_2 \ln X_2] \\
&= -R [X_1 \ln X_1 + (1 - X_1) \ln (1 - X_1)]
\end{aligned}$$

For entropy of mixing to be maximum, the first derivative $\frac{\delta(\Delta S_{\text{mixing}})}{\delta X_1}$ should be zero and the second derivative should be negative. Differentiating ΔS_{mixing} with respect to X_1 we get

$$\begin{aligned}
\frac{\delta(\Delta S_{\text{mixing}})}{\delta X_1} &= -R \left[\ln X_1 + \frac{X_1}{X_1} + \frac{1 - X_1}{1 - X_1} (-1) + (-1) \ln (1 - X_1) \right] \\
&= -R (\ln X_1 + 1 - 1 - \ln (1 - X_1)) = 0 \\
\text{or } \ln X_1 + 1 - 1 - \ln (1 - X_1) &= 0
\end{aligned}$$

$$\text{or } \ln \frac{X_1}{1-X_1} = 0 \quad \text{or } X_1 = 1 - X_1$$

$$2X_1 = 1 \quad X_1 = 1/2 = 0.5$$

And hence $X_2 = 1 - 0.5 = 0.5$.

Practice problems

- 1 mole of H_2 and 9 moles of N_2 are mixed at 298 K and 1 atmosphere. Assuming the ideal behavior of the gas, calculate the entropy of mixing per mole of the mixture formed.

[Ans 2.704 J K⁻¹ mol⁻¹]

15.21 Free Energy Function (G) and Work Function(A)

The feasibility of a process or chemical reaction cannot be determined by enthalpy change or entropy change alone. Both the functions are essential to predict the spontaneity or feasibility of a chemical reaction. The functions which incorporate both energy and entropy change are the free energy function and work function represented by G and A respectively. Both these functions are state functions, that is, their value depends only on the initial and final state of the system. They are given by

$$A = E - TS$$

$$G = H - TS$$

Physical significance of work function Consider an isothermal change from initial state denoted by subscript 1 to the final state denoted by the subscript 2.

$$A_1 = E_1 - TS_1 \quad \text{and} \quad A_2 = E_2 - TS_2$$

Change in work function at constant temperature is given by

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \tag{1}$$

$\therefore \Delta S = \frac{q_{\text{rev}}}{T}$, where q_{rev} is the heat taken up when the reaction is carried out in a reversible manner. Substituting the value of ΔS in Eq. (1) we get

$$\Delta A = \Delta E - q_{\text{rev}} \tag{2}$$

According to the first law of thermodynamics, for a reversible isothermal process

$$\Delta E = q + w \text{ hence}$$

$$w_{\text{rev}} = \Delta E - q_{\text{rev}}$$

If work is done by the system it is negative so that

$$-w_{\text{rev}} = \Delta E - q_{\text{rev}} \quad (3)$$

Comparing Eq. (2) and (3) we get,

$$-\Delta A = w_{\text{rev}}$$

Thus, at constant temperature decrease in the function A is equal to the reversible work done by the system. As reversible work is the maximum work that can be obtained from a given thermodynamic change in state, in an isothermal process the decrease in work function is a measure of the maximum work obtainable from the change in state. The work function A is also referred to as Helmholtz free energy or the Helmholtz function.

Similarly considering the free energy function G we have

$$G = H - TS$$

If at constant temperature the thermodynamic functions in the initial and final states are represented G_1, H_1, S_1 and G_2, H_2, S_2 respectively then

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S$$

As studied earlier at constant pressure

$$\begin{aligned} \Delta H &= \Delta E + P\Delta V \\ \therefore \Delta G &= \Delta E + P\Delta V - T\Delta S \end{aligned}$$

$$\text{or } \Delta G = \Delta A + P\Delta V \quad \therefore \Delta A = \Delta E - T\Delta S$$

Since ΔA is equal to $-w$ hence,

$$\Delta G = -w + P\Delta V \text{ or } -\Delta G = w - P\Delta V$$

Since $P\Delta V$ gives the work expansion of the gas at constant pressure hence the term $-\Delta G$ is a measure of work other than the work due to change in volume at constant temperature and pressure. This work other than the work due to the change in volume is termed as the net work, thus

$$\text{Net work} = w - P\Delta V = -\Delta G$$

The quantity ΔG is termed as the Gibbs free energy or simply free energy and $-\Delta G$ gives the decrease in free energy. Since ΔG measures work other than the work due to change in volume hence the net work is a measure of the electrical or chemical work.

Variation of free energy on pressure and temperature

By definition,

$$G = H - TS$$

Since $H = E + PV$

$$\therefore G = E + PV - TS.$$

By partial differentiation we get

$$dG = dE + PdV + VdP - TdS - SdT \quad (1)$$

From the first law of thermodynamics,

$$dq = dE - dw$$

If the work done is only due to expansion then

$$-dw = PdV$$

$$\therefore dq = dE + PdV$$

$$\text{or } dE = dq - PdV \quad (2)$$

It is assumed that the process is reversible and no work other than that of volume change is occurring, hence

$$dq = TdS$$

Substituting the value of dq in Eq. (2), we get

$$dE = TdS - PdV \quad (3)$$

Putting the value of dE in Eq. (1), we get

$$dG = VdP - SdT \quad (4)$$

This equation takes different forms under different conditions

(i) **At constant temperature**, that is, when $dT = 0$, Eq. (4) takes the form

$$\begin{aligned} dG &= VdP \\ \text{or } \left(\frac{\partial G}{\partial P} \right)_T &= V \end{aligned} \quad (5)$$

(ii) **At constant pressure**, that is, when $dP = 0$, Eq. (4) takes the form

$$\begin{aligned} dG &= -SdT \\ \text{or } \left(\frac{\partial G}{\partial T} \right)_P &= -S \end{aligned} \quad (6)$$

Free energy change with pressure for an ideal gas

At constant temperature, it follows that

$$dG = VdP \quad (7)$$

If the pressure changes from P_1 to P_2 , the corresponding free energy will change from G_1 to G_2 . Integrating Eq. (7) between these limits, we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP \quad (8)$$

for an ideal gas

$$V = \frac{nRT}{P}$$

Substituting the value of V in Eq. (8), we get

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{nRT}{P} dP$$

$$\text{or } \Delta G = G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\text{or } \Delta G = 2.303 nRT \log \frac{P_2}{P_1} = 2.303 nRT \log \frac{V_1}{V_2} \quad (9)$$

where V_1 and V_2 are the initial and final volumes, respectively. As G is a state function, Eq. (9) gives free energy change whether the reaction is carried out reversibly or irreversibly.

Solved examples

1. Calculate the free energy change when 4 moles of an ideal gas expands from a pressure of 10 to 1 atm at 25 °C.

Solution

$$\Delta G = 2.303 nRT \log \frac{P_2}{P_1}$$

Here, $n = 4$ moles; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $T = 273 + 25 = 298 \text{ K}$; $P_1 = 10 \text{ atm}$; $P_2 = 1 \text{ atm}$.

$$\begin{aligned} \Delta G &= 2.303 \times 4 \times 8.314 \times 298 \log \frac{1}{10} \\ &= -22823.39 \text{ J} \end{aligned}$$

2. ΔG for a reaction at 300 K is -16 kcal; ΔH for the reaction is -10 kcal. What is the entropy of the reaction? What will be ΔG at 330 K?

Solution

$$(i) \Delta G = \Delta H - T\Delta S$$

$$\text{or } \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-10 \text{ kcal} + 16 \text{ kcal}}{300 \text{ K}} = 0.02 \text{ kcal K}^{-1} = 20 \text{ cal K}^{-1}$$

$$(ii) \Delta G \text{ at } 330 \text{ K} = \Delta H - T\Delta S$$

$$= -10 \text{ kcal} - 330 \text{ K} \times 0.02 \text{ kcal K}^{-1} = -16.6 \text{ kcal.}$$

3. Calculate ΔG for the conversion of 1 mole of water at 100°C and 1 atm to steam at 100°C and 0.5 atm pressures.

Solution

$\Delta G = (\Delta G \text{ for the conversion of } \text{H}_2\text{O (l)} \text{ at } 100^\circ\text{C} \text{ and 1 atm to steam at } 100^\circ\text{C} \text{ and 1 atm}).$
 $+ (\Delta G \text{ for the transition of steam at } 100^\circ\text{C} \text{ from 1 atm to 0.5 atm}).$

The first term on the RHS is zero, as $\text{H}_2\text{O (l)}$ and $\text{H}_2\text{O (g)}$ are in equilibrium at 100°C and 1 atm pressure.

$$\text{The second term is } = 2.303 nRT \log \frac{P_2}{P_1}$$

$$\Delta G = 2.303 \times 1 \times 1.987 \times 373 \times \log_{10} \frac{0.5}{1}$$

$$= 2.303 \times 1 \times 1.987 \times 373 \times (-0.3010)$$

$$= -513.82 \text{ cal}$$

Practice problems

- 4 mole of an ideal gas is compressed isothermally at 300 K from $2.02 \times 10^5 \text{ N m}^{-2}$ to $4.04 \times 10^5 \text{ N m}^{-2}$ pressure. Calculate the free energy change for the process. [Ans 6916.63 J]
- One mole of an ideal gas at 27°C expands isothermally and reversibly from initial volume of 2 dm^3 to a final volume of 20 dm^3 against a pressure that is gradually reduced. Calculate q , w , ΔE , ΔH , ΔA , ΔG and ΔS .
 [Ans $q = 5744 \text{ J mol}^{-1}$; $w = -5744 \text{ J mol}^{-1}$; $\Delta E = 0$; $\Delta H = 0$; $\Delta A = -5744 \text{ J mol}^{-1}$.
 $\Delta G = -5744 \text{ J mol}^{-1}$ and $\Delta S = 19.15 \text{ J K}^{-1} \text{ mol}^{-1}$]
- Calculate ΔG for the formation of $\text{H}_2\text{O (l)}$ from its elements at 25°C . $\Delta H_f = -286 \text{ kJ}$. Entropies of $\text{H}_2 \text{ (g)}$, $\text{O}_2 \text{ (g)}$ and $\text{H}_2\text{O (g)}$ are 130.6, 205.0 and $70.3 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.
 [Ans $\Delta G = -237.5 \text{ kJ}$]

15.22 Gibbs–Helmholtz Equation

At constant pressure, the change of free energy with temperature is given by

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (10)$$

Suppose a system changes reversibly and isothermally from state 1 to state 2. If the free energy and entropy of the system in state 1 are G_1 and S_1 respectively, and in state 2 are G_2 and S_2 respectively, then the entropy change of the system is given by

$$\Delta S = S_2 - S_1 \quad (11)$$

From Eq. (10) we can write

$$S_1 = -\left(\frac{\partial G_1}{\partial T}\right)_p \quad \text{and} \quad S_2 = -\left(\frac{\partial G_2}{\partial T}\right)_p$$

Substituting the values of S_1 and S_2 in Eq. (11) we get

$$\begin{aligned} \Delta S &= -\left[\left(\frac{\partial G_2}{\partial T}\right)_p - \left(\frac{\partial G_1}{\partial T}\right)_p\right] \\ \text{or } \Delta S &= -\left(\frac{\partial(G_2 - G_1)}{\partial T}\right)_p \\ \text{Or } \Delta S &= -\left(\frac{\partial \Delta G}{\partial T}\right)_p \end{aligned} \quad (12)$$

For an isothermal process, $\Delta G = \Delta H - T\Delta S$

Substituting the value of ΔS from Eq. (12) in this equation we get,

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \quad \dots\dots(13) \quad (13)$$

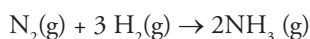
This equation was derived by J.W. Gibbs and H. Von Helmholtz and is known as the **Gibbs–Helmholtz equation**

A corresponding equation for the work function A and internal energy E for an isothermal reversible process at constant volume yields another form of the Gibbs–Helmholtz equation –

$$\Delta A = \Delta E + T\left(\frac{\partial \Delta A}{\partial T}\right)_v \quad (14)$$

Solved problems

1. For the following reaction



The free energy change at 25 °C and 35 °C are -3.98 and -3.37 kcal. Calculate the heat of reaction at 35 °C.

Solution

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p$$

$$\text{also } \left(\frac{\partial \Delta G}{\partial T} \right)_p = \frac{G_2 - G_1}{T_2 - T_1}$$

Here $G_1 = -3.98$ kcal; $G_2 = -3.37$ kcal

$$T_1 = 273 + 25 = 298 \text{ K}; \quad T_2 = 273 + 35 = 308 \text{ K}$$

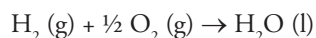
$$\therefore \left(\frac{\partial \Delta G}{\partial T} \right)_p = \frac{-3.37 - (-3.98)}{308 - 298} = \frac{0.61}{10} = 0.061$$

At 35 °C $\Delta G = -3.37$ kcal; $T = 308$ K.

$$-3.37 = \Delta H + 308(0.061)$$

$$\Delta H = -3.37 - 18.79 = -22.16 \text{ kcal}$$

2. For the following reaction



The value of enthalpy change and free energy change are -68.32 and -56.69 kcal respectively at 25 °C. Calculate the value of free energy change at 30 °C.

Solution

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p$$

Here $\Delta G = -56.69$ kcal; $\Delta H = -68.32$ kcal $T = 273 + 25 = 298$ K

$$\therefore \left(\frac{\partial \Delta G}{\partial T} \right)_p = \frac{-56.69 + 68.32}{298} = 0.039$$

Assuming that $\left(\frac{\partial \Delta G}{\partial T} \right)_p$ remains constant over this range of temperature, at 30 °C we can write

$$\begin{aligned} \Delta G &= -68.32 + 303 \times 0.039 \\ &= -68.32 + 11.81 \\ &= -56.51 \text{ kcal} \end{aligned}$$

Practice problems

1. The free energy change for a reaction is -86.5 kJ per mole at 298 K and -83.50 kJ per mole at 308 K. Calculate the enthalpy change (ΔH) for the reaction at 303 K.
[Ans = -175.9 kJ]
2. Calculate ΔA and ΔG for the reversible compression of one mole of an ideal gas from 2 atm to 100 atm at 30.2°C .
[Ans $\Delta A = 2357.25$ cal; $\Delta G = 2357.25$ cal]

15.23 Claypeyron–Clausius Equation

This equation finds application in one component and in the two-phase systems. Let us consider two phases A and B of the same component in equilibrium with each other at constant temperature T and pressure P . This equilibrium may be represented as



Suppose free energies per mole of the substance in the two phases A and B are G_A and G_B , respectively. As the system is in equilibrium, there is no change in free energy, that is,

$$G_A = G_B \quad (1)$$

If the temperature is raised to $T + dT$, the pressure P will increase to $P + dP$. For this change, the molar free energy becomes $G_A + dG_A$ and $G_B + dG_B$, respectively.

As the two phases are in equilibrium,

$$G_A + dG_A = G_B + dG_B \quad (2)$$

As for this phase change the work done is only because of the volume change, the change in energies dG_A and dG_B may be calculated by the equation

$$dG = V.dP - S.dT \quad (3)$$

Therefore, it can be written as

$$dG_A = V_A dP - S_A dT \quad (4)$$

$$dG_B = V_B dP - S_B dT \quad (5)$$

V_A and V_B are the molar volumes of the phases A and B respectively, and S_A and S_B are their corresponding enthalpies. Hence,

$$V_A dP - S_A dT = V_B dP - S_B dT$$

$$\text{or } \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A} \quad (6)$$

where ΔS = molar entropy change and $V_B - V_A$ is the change in volume when 1 mole of substance changes from A to B.

From Gibbs–Helmholtz equation

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

∴ $\Delta G = 0$ (Eq. 1). Hence, Eq. (7) may be written as

$$\Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta S = \frac{\Delta H}{T} \quad \dots (8)$$

Placing this in Eq. (6) we get

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_B - V_A)}, \quad (9)$$

This is the Claypeyron – Clausius equation. ΔH represents the change in enthalpy for phase change at temperature T and $\frac{dP}{dT}$ represents the rate of change of pressure with temperature.

Integrated form of Claypeyron – Clausius equation for liquid – vapor equilibrium

In liquid vapor equilibrium $V_v \gg V_L$, hence $V_v - V_L \approx V_v$

The Claypeyron–Clausius equation takes the form

$$\frac{dP}{dT} = \frac{\Delta H_v}{TV_v} \quad (10)$$

Assuming the vapours behave ideally,

$$PV_v = RT \quad \text{or} \quad V_v = \frac{RT}{P}$$

Inserting this value in Eq. (10)

$$\frac{1}{P} \frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

Integrating, on the assumption that ΔH_v is constant over a small temperature change, we get

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where P_1 and P_2 are the vapor pressures at T_1 and T_2 respectively. Molar heat of vaporisation at different temperatures can be computed with this equation.

Solved examples

1. The latent heat of vaporisation of benzene at its boiling point (80 °C) is 7413 cal mol⁻¹. What is the vapor pressure of benzene at 27 °C.

Solution

$$\Delta H_v = 7413 \text{ cal mol}^{-1} ; T_1 = 80^\circ\text{C} = 353 \text{ K}; P_1 = 1 \text{ atm} = 760 \text{ mm Hg}$$

$$T_2 = 27^\circ\text{C} = 300 \text{ K}; P_2 = ?$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\begin{aligned} \log \frac{P_2}{760 \text{ mm Hg}} &= \frac{7413 \text{ cal mol}^{-1}}{2.303 \times 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}} \left[\frac{300 - 353}{300 \times 353} \right] \\ &= \frac{7413 \times (-53)}{2.303 \times 1.987 \times 300 \times 353} = -0.8107 \end{aligned}$$

$$\log \frac{760 \text{ mm Hg}}{P_2} = 0.8107$$

$$\text{or } \frac{760 \text{ mm Hg}}{P_2} = \text{Antilog } 0.8107 = 6.4670$$

$$\text{Hence } P_2 = 760 / 6.4670 = 117.52 \text{ mm Hg}$$

2. If the atmospheric pressure is 535 mm of mercury, find the temperature at which water will boil. Latent heat of vaporisation of water is 545.5 cal/g.

Solution

$$P_1 = 535 \text{ mm Hg} ; P_2 = 1 \text{ atm} = 760 \text{ mm Hg}$$

$$T_1 = ? ; T_2 = 100 + 273 = 373 \text{ K}$$

$$\Delta H_v = 545.5 \text{ cal/g} = 545.5 \times 18 \text{ cal/mol} = 9819 \text{ cal mol}^{-1}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \frac{760}{535} = \frac{9819 \text{ cal mol}^{-1}}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left[\frac{1}{T_1} - \frac{1}{373} \right]$$

$$\frac{1}{T_1} - \frac{1}{373} = \frac{0.1524 \times 2.303 \times 1.987}{9819} = 0.00007102$$

$$\text{or } \frac{1}{T_1} - 0.002681 \text{ K}^{-1} = 0.00007102 \text{ K}^{-1}$$

$$T_1 = \frac{1}{0.00275202} = 363.37 \text{ K}$$

Practice problems

1. The latent heat of vaporisation of water is 540 cal/g at about 100 °C. Calculate the pressure at which water must be heated to produce superheated steam at 150 °C. [Ans 4.709 atm]

15.24 Vant Hoff Isotherm

Consider the general reaction



We know that

$$dG = VdP - SdT$$

$$\text{At constant temperature } (dG)_T = VdP$$

The free energy change for 1 mole of any gas at constant temperature is given by

$$dG = VdP \quad \because \text{for an ideal gas } PV = RT \text{ or } V = RT/P$$

$$\text{Hence } dG = RT \cdot \frac{dP}{P}$$

Integrating,

$$\begin{aligned} \int dG &= RT \int \frac{dP}{P} \\ G &= G^\circ + RT \ln P \end{aligned} \quad (2)$$

Here, G° is the integration constant and is known as the standard free energy, that is, $G^\circ = G$ when $P = 1$ atm.

Let the free energy per mole of A, B, C, D at their respective pressures P_A, P_B, P_C, P_D are G_A, G_B, G_C, G_D respectively. Then the free energy of A per mole at temperature T is

$$G_A = G_A^\circ + RT \ln P_A$$

Similarly, free energies of B, C and D are as follows:

$$G_B = G_B^\circ + RT \ln P_B$$

$$G_C = G_C^\circ + RT \ln P_C$$

$$G_D = G_D^\circ + RT \ln P_D$$

The change in free energy ΔG is

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = [(G_C + G_D) - (G_A + G_B)]; \text{ hence,}$$

$$\Delta G = (G_C^\circ + RT \ln P_C + G_D^\circ + RT \ln P_D) - (G_A^\circ + RT \ln P_A + G_B^\circ + RT \ln P_B)$$

$$= (G_C^\circ + G_D^\circ - G_A^\circ - G_B^\circ) + RT \ln \frac{P_C \times P_D}{P_A \times P_B}$$

$$G = \Delta G^\circ + RT \ln \frac{P_C \times P_D}{P_A \times P_B} \quad (3)$$

ΔG^0 = Standard free energy of reaction (1);

but at equilibrium $\Delta G = 0$.

Therefore, $0 = \Delta G^0 + RT \ln K_{eq}$

$$\text{or } \Delta G^0 = -RT \ln K_{eq} \quad \dots\dots 4 \quad (4)$$

$$\text{where } K_{eq} = \frac{P_C \times P_D}{P_A \times P_B}$$

On substituting this value of ΔG^0 in Eq. (3)

$$\Delta G = -RT \ln K_{eq} + RT \ln \frac{P_C \times P_D}{P_A \times P_B} \quad (5)$$

For the general reaction; $aA + bB \rightarrow cC + dD$; the Eq. (5) becomes

$$\Delta G = -RT \ln K_{eq} + RT \ln \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \quad (6)$$

This expression is termed as the Van't Hoff isotherm. It gives a quantitative relationship for the free energy change in a chemical reaction.

Van't Hoff isochore It deals with the variation of equilibrium constant with temperature.

$$\Delta G^0 = -RT \ln K_{eq}$$

$$\ln K_{eq} = -\frac{\Delta G^0}{RT} = \frac{-(\Delta H^0 - T\Delta S^0)}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

$$\therefore \ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \quad \text{and} \quad \ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

$$\text{or } \ln K_2 - \ln K_1 = \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H^0}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \text{or}$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^0}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad (7)$$

This expression, called the Van't Hoff isochore, can be used to calculate equilibrium constant at T_2 if its value at T_1 is known.

Solved example

1. The equilibrium constant for the reaction

$H_2(g) + S(s) \rightleftharpoons H_2S(g)$ is 18.5 at 925 K and 9.25 at 1000 K. Calculate standard enthalpy of the reaction. Also calculate ΔG^0 and ΔS^0 at 925 K.

Solution

From Van't Hoff isochore,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log \frac{K_{1000K}}{K_{925K}} = \frac{\Delta H^\circ}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1000 - 925}{925 \times 1000} \right)$$

$$\log \frac{9.25}{18.5} = \frac{\Delta H^\circ}{2.303 \times 8.314} \left(\frac{75}{925000} \right)$$

$$\Delta H^\circ = -71080 \text{ J mol}^{-1} = -71.08 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{now; } \Delta G^\circ &= -2.303RT \log K_{\text{eq}} \\ &= -2.303 \times 8.314 \text{ J mol}^{-1} \times 925 \log 18.5 \\ &= -22400 \text{ J mol}^{-1} \\ &= -22.4 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= \frac{\Delta H^\circ - \Delta G^\circ}{T} \\ &= \frac{(-71080 + 22400) \text{ J mol}^{-1}}{925} = -52.6 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Practice problems

1. The equilibrium constant of the reaction $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ at 528°C is 98.0 and at 680°C is 10.5. Find the heat of reaction. [Ans - 93273.33 J]
2. The equilibrium constant K for the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is 1.064×10^{-4} at 400°C and 0.144×10^{-4} at 500°C . Calculate the mean heat of formation of 1 g mol of ammonia from its elements in this temperature range. [Ans $\Delta H = -12575 \text{ cal}$]

15.25 Maxwell's Thermodynamic Relations**We know that**

$$H = E + PV$$

$$A = E - TS.$$

$$\text{and } G = H - TS \quad \text{or} \quad G = E + PV - TS$$

The differential forms of these equations can be written as

$$dH = dE + PdV + VdP \quad (1)$$

$$dA = dE - TdS - SdT \quad (2)$$

$$dG = dE + PdV + VdP - TdS - SdT \quad (3)$$

As $dE = TdS - PdV$, substituting the value of dE in Eqs. (1), (2) and (3), we get

$$dH = TdS + VdP \quad (4)$$

$$dA = -SdT - PdV \quad (5)$$

$$dG = VdP - SdT \quad (6)$$

The above three Eqs. (4), (5) and (6) along with the equation $dE = TdS - PdV$ are the four fundamental equations of thermodynamics.

Derivation of Maxwell's equations

If an exact differential dZ can be put in the form $dZ = Mdx + Ndy$ then $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ is

known as the Euler's relation. This can be used to obtain the Maxwell's relations.

From the fundamental thermodynamic equations, we have

$$dH = TdS + VdP$$

compare with $dZ = Mdx + Ndy$

By the Euler relation,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (7)$$

$$dA = -SdT - PdV$$

using Euler's relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (8)$$

$$dG = VdP - SdT$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \quad (9)$$

on comparing with Euler's relation we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (10)$$

These above four equations are known as Maxwell's relations. The relations (8) and (9) are referred to as isothermal relations and the relations (7) and (10) are isentropic or adiabatic.

15.26 Spontaneity and Equilibrium

Equilibria and spontaneity change can be explained in terms of various thermodynamic functions. Entropy (S) and free energy (G) are the important thermodynamic functions used for predicting equilibrium.

Entropy as a criterion of equilibrium and spontaneity change

By the first law of thermodynamics $dq = dE + PdV$, where dq is the quantity of heat absorbed and dE is the change in the internal energy of the system and PdV , the mechanical work done by the system. Suppose the process is reversible

$$\begin{aligned} dq_{\text{rev}} &= dE + (PdV)_{\text{rev}} \\ \text{but, } dS &= \frac{dq_{\text{rev}}}{T} \quad \therefore dS = \frac{dE + (PdV)_{\text{rev}}}{T} \end{aligned} \quad (1)$$

If the process is irreversible, then

$$\frac{dq_{\text{irrev}}}{T} = \frac{dE + (PdV)_{\text{irrev}}}{T} \quad (2)$$

In both these expressions, dE is the same, as E is a thermodynamic property that depends only on the initial and final states of the system and not on the path, whether reversible or irreversible.

If the reversible process occurs at constant internal energy (E) and volume (V), then from equation, $\partial S_{E,V} = 0$. As the condition for reversible change is also the condition for equilibrium, we have

$$\partial S_{E,V} = 0 \quad (3)$$

Comparing the right hand sides of the Eqs. (1) and (2), $(PdV)_{\text{rev}} > (PdV)_{\text{irrev}}$, as for the given initial and final states, the work done is maximum for a reversible process.

$$\begin{aligned} \therefore dS &> \frac{dq_{\text{irrev}}}{T} \quad \text{or} \quad dS > \frac{dE + (PdV)_{\text{irrev}}}{T} \\ \text{or} \quad \partial S_{E,V} &> 0 \end{aligned} \quad (4)$$

This is the condition for a spontaneous process. Equations (3) and (4) are combined and the condition for spontaneous change and equilibrium are expressed as

$$\partial S_{E,V} \geq 0$$

In an analogous manner, it would follow from Eqs. (1) and (2), that for equilibrium $\partial S_{E,V} = 0$ and for a spontaneous process $\partial S_{E,V} < 0$. Combining the two conditions,

$$\partial S_{E,V} \leq 0$$

Thus, in any spontaneous process taking place at constant E and V , the entropy increases ultimately reaching a maximum value at equilibrium. Once the equilibrium is reached, there occurs no more change in entropy. A system with constant E and V is also known as an isolated system and the universe is one such system. As spontaneous processes continuously occur in the universe, the entropy of the universe is increasing.

Similarly, in any spontaneous process taking place at constant S and V , the internal energy goes on decreasing, ultimately attaining a minimum value at equilibrium.

Gibbs free energy (G) as a criterion of equilibrium and spontaneous change

By definition,

$$\begin{aligned} G &= H - TS \\ &= E + PV - TS \end{aligned}$$

where H is the enthalpy of the system

For an infinitesimal change,

$$\begin{aligned} dG &= dE + PdV + VdP - TdS - SdT \\ &= \underbrace{VdP - SdT}_{\text{I term}} + \underbrace{dE + PdV - TdS}_{\text{II term}} \end{aligned}$$

At constant temperature and pressure, the first term becomes zero and hence $\partial G_{T,P} = dE + PdV - TdS$. If we assume the work done by the system to be work of expansion (PdV) then

$$dq = dE + PdV$$

$\therefore \partial G_{T,P} = dq - TdS$. If the process is reversible then $dq = dq_{\text{rev}} = TdS$ and hence

$$\partial G_{T,P} = 0$$

As already indicated, the condition for a reversible process is also a condition for equilibrium, hence for equilibrium

$$\partial G_{T,P} = 0$$

$$dq_{\text{rev}} = dE + (PdV)_{\text{rev}} \quad \text{and}$$

$$dq_{\text{irrev}} = dE + (PdV)_{\text{irrev}}$$

$$\text{since } (PdV)_{\text{rev}} > (PdV)_{\text{irrev}}$$

$$\text{Hence } dq_{\text{rev}} > dq_{\text{irrev}}$$

Consider the expression-

$$\partial G_{T,P} = dq - TdS$$

For irreversible process.

$$\partial G_{T,P} = dq_{\text{irrev}} - TdS$$

$$\text{But, } dq_{\text{irrev}} < dq_{\text{rev}}$$

$$\text{and } dq_{\text{rev}} = TdS$$

$$\therefore dq_{\text{irrev}} < TdS$$

Hence, for an irreversible or spontaneous process and equilibrium $\partial G_{T,P} < 0$

Combining the conditions for spontaneous process and equilibrium,

$$\partial G_{T,p} \leq 0$$

Thus, for any spontaneous process taking place at constant temperature and pressure, the free energy of the system decreases, ultimately attaining a minimum value at equilibrium.

In an analogous manner, the conditions for spontaneous change and equilibrium can be expressed in terms of the Helmholtz free energy (A) as

$$\partial A_{T,V} \leq 0 \quad \text{where} \quad A = E - TS$$

Entropy and free energy criteria compared

The free energy criteria for spontaneous change and equilibrium are more useful than the entropy criteria. Recapitulating these criteria,

$$\partial S_{E,V} \geq 0 \quad \text{and} \quad \partial G_{T,p} \leq 0$$

It is difficult to keep internal energy of a system constant, whereas the temperature and pressure can be easily kept constant. Hence, G has a greater utility. This point can be viewed in an alternative manner. A system with constant E , V is an isolated system, which may be taken to constitute both the system and the surrounding. Hence, in using the entropy criterion, it is essential to make measurements on both system and surroundings. However, it is rather difficult to make measurement on the surroundings. Hence, the criterion of entropy is less useful.

Solved examples

1. Enthalpy and entropy changes of a reaction are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Predict the feasibility of the reaction at 27°C .

Solution

$$\Delta H = 40.63 \text{ kJ mol}^{-1} = 40630 \text{ J mol}^{-1}; \quad \Delta S = 108.8 \text{ J K}^{-1} \text{ mol}^{-1}; \quad T = 27+273 = 300 \text{ K}$$

$$\Delta G = \Delta H - T\Delta S$$

$$= 40630 - 300 \times 108.8 = +7990 \text{ J mol}^{-1} = 7.99 \text{ kJ mol}^{-1}$$

As ΔG is positive, the reaction is not feasible.

2. ΔH and ΔS for the reaction,
 $\text{Ag}_2\text{O (s)} \rightarrow 2\text{Ag(s)} + \frac{1}{2} \text{O}_2 \text{ (g)}$
 are $30.56 \text{ kJ mol}^{-1}$ and $66.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Calculate the temperature at which the free energy change for the reaction will be zero. Predict whether the forward reaction will be favored above or below this temperature.

Solution

According to Gibb Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium, $\Delta G = 0$ so that

$$0 = \Delta H - T\Delta S \quad \text{or} \quad \Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} \quad \text{Here, } \Delta H = 30.56 \text{ kJ mol}^{-1} = 30560 \text{ J mol}^{-1} \quad \text{and } \Delta S = 66 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = \frac{30560}{66} = 463 \text{ K}$$

In the above reaction, both ΔH and ΔS are positive, therefore the reaction will be spontaneous above 463 K, so that the term $T\Delta S$ becomes greater than ΔH and ΔG becomes negative.

Practice problems

- For the melting of ice at 25 °C, $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$

The enthalpy of fusion is 6.97 kJ mol⁻¹ and entropy of fusion is 25.4 J mol⁻¹ K⁻¹. Calculate the free energy change and predict whether the melting of ice is spontaneous or not at this temperature.

[Ans $\Delta G = -0.6 \text{ kJ mol}^{-1}$. As ΔG is negative, hence the reaction is spontaneous]

- The values of ΔH and ΔS for two reactions are given below

Reaction A $\Delta H = -10.5 \times 10^3 \text{ J mol}^{-1}$

$$\Delta S = +31 \text{ J K}^{-1} \text{ mol}^{-1}$$

Reaction B $\Delta H = -11.7 \times 10^3 \text{ J mol}^{-1}$

$$\Delta S = -105 \text{ J K}^{-1} \text{ mol}^{-1}$$

Predict whether these reactions are spontaneous or not at 298 K.

[Ans Reaction A: spontaneous; reaction B: non-spontaneous]

Summary

Important thermodynamic relations

- $\Delta E = q + w$

Heat (q) absorbed by the system = + q

Heat released to the surrounding = - q

Work done by the system (work expansion) = -w

Work done on the system (work compression) = +w.

- $\Delta H = \Delta E + P\Delta V$

$$q_p = q_v + P\Delta V$$

$$3. \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p, \quad C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

For an ideal gas

- $\left(\frac{\partial E}{\partial P} \right)_T = 0, \left(\frac{\partial E}{\partial V} \right)_T = 0, \left(\frac{\partial H}{\partial P} \right)_T = 0, \left(\frac{\partial H}{\partial V} \right)_T = 0$
- $PV = nRT$
- $C_p - C_v = R$

Isothermal process for an ideal gas

- $\Delta E = 0; \Delta H = 0, q = w$
- $w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2} = -2.303nRT \log_{10} \frac{V_2}{V_1}$
- $w_{\text{irrev}} = - \int_{V_1}^{V_2} P dV = -P(V_2 - V_1) = nRT \left(1 - \frac{P_1}{P_2} \right)$
- Work done in isochoric process = 0 $\because dV = 0$
- Work done against zero external pressure = 0 (if a gas expands against vacuum no work is done).

Adiabatic processes for an ideal gas

- $w = \Delta E \quad \because q = 0$
- **For reversible process,**
- $PV^\gamma = \text{constant}; TV^{\gamma-1} = \text{constant}; T^\gamma / P^{\gamma-1} = \text{constant}$
- **Work done in a reversible process**

$$\bullet \quad w = nC_v T_1 \left(\left(\frac{V_1}{V_2} \right)^{\frac{R}{C_v}} - 1 \right)$$

$$\bullet \quad w = nC_v T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

$$\bullet \quad w = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$\bullet \quad R = C_p - C_v$$

- $\gamma = \frac{C_p}{C_v}$
- γ for a monoatomic gas = 5/3.
- For monoatomic gas $C_p = 5 \text{ cal K}^{-1} \text{ mol}^{-1}$; $C_v = 3 \text{ cal K}^{-1} \text{ mol}^{-1}$
- $-w_{\text{irrev}} = nRT_1 \left(\frac{T_2}{T_1} - \frac{P_2}{P_1} \right)$
- $\Delta E = P_2 \left(\frac{nRT_1}{P_1} - \frac{nRT_2}{P_2} \right)$
- $\Delta H = C_p (T_2 - T_1) = nRT_1 \left(\frac{P_2 - P_1}{P_1} \right)$
- Work (isothermal) > Work (adiabatic)
- **Kirchhoff's equation** = $\left[\frac{\partial(\Delta H)}{\partial T} \right]_p = \Delta C_p$
- $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p (T_2 - T_1)$
- Joule-Thomson co-efficient $\mu_{J,T} = \left(\frac{\partial T}{\partial P} \right)_H$
- **Second law of thermodynamics**

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat drawn from the source}} = \frac{q_1 - q_2}{q_1}$$

$$= \frac{RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_4}{V_3}}{RT_1 \ln \frac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1} = \frac{q_1 - q_2}{q_1} = \frac{w}{q_1}$$

Entropy

- $\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T}$
- $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$; $\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f}$
- $\Delta S_{\text{tran}} = \frac{q_{\text{rev}}}{T}$

Entropy changes for an ideal gas

- $\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$
- $\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$
- For isothermal process $\Delta S_T = nR \ln \frac{V_2}{V_1} = nR \ln \frac{P_1}{P_2}$
- For isobaric process $\Delta S_p = nC_p \ln \frac{T_2}{T_1}$
- For isochoric process $\Delta S_v = nC_v \ln \frac{T_2}{T_1}$
- Entropy change in heating a solid or liquid $\Delta S = ms \ln \frac{T_2}{T_1}$
- Entropy of mixing. $S_{\text{mix}} = -R \sum n_i \ln X_i$

Free energy

- $\Delta G = \Delta H - T\Delta S$

For ideal gas

- $dG = VdP - SdT$
- $\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$

Gibb's Helmholtz equation

- $\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T} \right)_p$

Another form

- $\Delta A = \Delta E + T \left(\frac{\partial \Delta A}{\partial T} \right)_v$

Fundamental thermodynamic equations

- $dE = TdS - PdV$
- $dH = TdS + VdP$
- $dA = -SdT - PdV$
- $dG = -SdT + VdP$

Maxwell's relations**Adiabatic or isentropic**

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

For isothermal

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Spontaneity and equilibrium

For spontaneity and equilibrium

$$\partial S_{E,V} \geq 0$$

$$\partial E_{S,V} \leq 0$$

$$\partial G_{T,P} \leq 0$$

$$\partial A_{T,V} \leq 0$$

Claypeyron–Clausius equation

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_B - V_A)}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_V}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Vant Hoff isotherm

$$\Delta G = -RT \ln K_{eq} + RT \ln \frac{P_C \times P_D}{P_A \times P_B}$$

Vant Hoff isochore

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Review Questions

- Distinguish between
 - Open system and closed system
 - Isothermal process and adiabatic process
 - Extensive properties and intensive properties
 - Reversible process and irreversible process
 - Homogeneous system and heterogeneous system
 - Isobaric and isochoric processes.
- State and explain the first law of thermodynamics
- What do you understand by the term 'Internal energy' and 'Enthalpy' of a system. Show that the heat absorbed by a system at constant volume is equal to the increase in its internal energy, while that absorbed at constant pressure is equal to the increase in enthalpy.
- What is meant by thermodynamically reversible and irreversible processes? Show that the work done by a system is maximum when it is expanded isothermally and reversibly.
- Define work. Prove that the work done is path-dependent.
- Define heat capacity of a system. Show from thermodynamical considerations that for an ideal gas
 - $C_v = dE/dT$
 - $C_p = dH/dT$
- Obtain different relationships between C_p and C_v for any system and then prove that $C_p - C_v = R$ for one mole of an ideal gas.
- For an ideal gas, prove that
 - $\left(\frac{\partial E}{\partial P}\right)_T = 0$
 - $\left(\frac{\partial E}{\partial V}\right)_T = 0$
 - $\left(\frac{\partial H}{\partial P}\right)_T = 0$
- In an adiabatic reversible expansion of an ideal gas show that
 - $PV^\gamma = \text{constant}$
 - $PV^{\frac{R}{C_v}} = \text{constant}$
 - $T^\gamma / P^{\gamma-1} = \text{constant}$

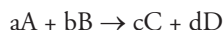
10. Show that the work of an adiabatic reversible expansion of an ideal gas is less than that of an isothermal reversible expansion.
11. Define the following terms
 - (i) Heat of reaction
 - (ii) Heat of formation
 - (iii) Heat of combustion
 - (iv) Heat of neutralisation
 - (v) Heat of solution
 - (vi) Heat of fusion
 - (vii) Heat of vaporisation
 - (viii) Heat of sublimation
12. State and explain the following laws of thermochemistry
 - (i) Lavoisier and Laplace's laws
 - (ii) Hess's law of constant heat summation.
13. Derive the Kirchhoff equation. Explain how it can be utilized to find out the heat of reaction at one temperature if the heat of reaction at another temperature is known.
14. What is enthalpy of a system? How is it related to internal energy? What is the relationship between ΔH and ΔE ?
15. Show that Joule–Thomson porous plug experiment is isenthalpic. Obtain an expression for Joule–Thomson coefficient and comment on its sign.
16. What are Joule–Thomson coefficient and inversion temperature? How would an ideal gas behave in a Joule–Thomson experiment?
17. Explain the following
 - (i) Entropy and its physical significance
 - (ii) Free energy and its physical significance
 - (iii) Spontaneous and non-spontaneous processes
18. Give the various statements of the second law of thermodynamics and show that all of them lead to the same goal.
19. Derive the concept of entropy from the second law of thermodynamics.
20. Derive the expression for the efficiency of the heat engine with the help of Carnot's cycle. Prove that the efficiency of a heat engine is always less than unity.
21. Derive the following expression for the change in entropy of an ideal gas
$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$
22. Prove thermodynamically that in an isothermal spontaneous expansion process the entropy is always increasing.
23. Derive an expression for the entropy change during mixing of ideal gases.

24. Derive the Gibbs–Helmholtz equation

25. Prove that

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

26. What is meant by Van't Hoff reaction? Derive an expression for the reaction isotherm of the general reaction.



27. Explain the concept of Helmholtz free energy and Gibb's free energy. Describe the relationship between the two.

28. If $dE = TdS - PdV$, prove that

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

29. What is spontaneity of a reaction? Describe the criteria for a chemical reaction to be spontaneous.

30. Derive the various forms of Maxwell's relations.

Multiple Choice Questions

- A wall which allows neither matter nor energy to pass through it is called
 - A rigid wall
 - An impermeable wall
 - Adiabatic wall
 - Diathermal wall
- Which of the following is not an intensive property
 - Volume
 - Pressure
 - Temperature
 - Viscosity
- Which of the following is not a extensive property
 - Heat capacity
 - Enthalpy
 - Entropy
 - Chemical potential
- A thermodynamic process occurring at constant temperature is
 - Isobaric process
 - Isochoric process
 - Isothermal process
 - Adiabatic process
- When a gas is subjected to adiabatic expansion, it gets cooled due to
 - Loss of kinetic energy
 - Fall in temperature
 - Decrease in velocity
 - Energy is used in doing work

6. Which of the following expresses the first law of thermodynamics
- (a) $w = q + \Delta E$ (b) $\Delta E = q + w$
(c) $q = E_2 - E_1 + w$ (d) All of the above
7. For a reversible process the value of ΔS is given by the expression
- (a) q_{rev} / T (b) $T + q_{\text{rev}}$
(c) $\Delta H / \Delta T$ (d) $q_{\text{rev}} \times T$
8. Heat and temperature are
- (a) Intensive properties
(b) Extensive properties
(c) Extensive and intensive properties respectively
(d) None of the above
9. According to the second law of thermodynamics heat is partly converted into useful work and part of it
- (a) Changes into kinetic energy
(b) Changes into electric energy
(c) Is always wasted
(d) None of the above
10. Which of the following expressions is not correct
- (a) $\gamma = \frac{C_p}{C_v}$ (b) $TV^{\gamma-1} = \text{constant}$
(c) $\frac{P}{V^\gamma} = \text{constant}$ (d) $\frac{T^\gamma}{P^{\gamma-1}} = \text{constant}$
11. For a gaseous reaction, $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$
- (a) $\Delta H > \Delta E$ (b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$ (d) $\Delta H = 0$
12. For the reaction $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$; the change in enthalpy is called
- (a) Heat of reaction (b) Heat of formation
(c) Heat of neutralisation (d) Heat of combustion
13. The enthalpies of combustion of C and CO are -390 kJ mol^{-1} and -278 kJ mol^{-1} respectively. The enthalpy of formation of CO is
- (a) 668 kJ mol^{-1} (b) 112 kJ mol^{-1}
(c) -112 kJ mol^{-1} (d) -668 kJ mol^{-1}
14. The enthalpies of formation of N_2O and NO are 82 and 90 kJ mol^{-1} . The enthalpy of reaction $2\text{N}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 4\text{NO}(\text{g})$ is
- (a) 8 kJ (b) -16 kJ
(c) 88 kJ (d) 196 kJ

15. Calculate the temperature at which $\Delta G = 5.2 \text{ kJ mol}^{-1}$, $\Delta H = 145.6 \text{ kJ mol}^{-1}$ and $\Delta S = 116 \text{ kJ mol}^{-1} = 116$ for a chemical reaction
- (a) 130 K (b) 1210 K
(c) 1300 °C (d) 130 °C
16. Which of the following process has a negative value of ΔS
- (a) Decomposition of lime (b) Dissociation of sugar in water
(c) Evaporation of water (d) Stretching of rubber band
17. One liter–atmosphere is nearly equal to
- (a) 185.0 J (b) 101.3 J
(c) 8.31 J (d) 4.18 J
18. A temperature at which gas becomes cooler on expansion is called
- (a) Inversion temperature (b) Critical temperature
(c) Boyle temperature (d) Transition temperature
19. Which of the following is not a state function
- (a) Internal energy (b) Entropy
(c) Work (d) Heat absorbed under isochoric conditions
20. The free energy $\Delta G = 0$ when
- (a) The system is at equilibrium (b) Catalyst is added
(c) Reactants are initially mixed thoroughly (d) Reactants are completely consumed
21. An endothermic reaction $A \rightarrow B$ proceeds spontaneously. The correct statement is
- (a) ΔH is positive and $T\Delta S > \Delta H$ (b) ΔH is positive and $\Delta H > T\Delta S$
(c) ΔS is negative and $T\Delta S > \Delta H$ (d) ΔG and ΔH both are negative
22. Consider the reactions
- (i) $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ $\Delta H = -68.39 \text{ kcal}$
(ii) $\text{K} + \text{H}_2\text{O} + \text{aq} \rightarrow \text{KOH(aq)} + \frac{1}{2} \text{H}_2$ $\Delta H = -48 \text{ kcal}$
(iii) $\text{KOH} + \text{aq} \rightarrow \text{KOH (aq)}$ $\Delta H = -14 \text{ kcal}$
- The heat of formation of KOH is
- (a) $-68.39 + 48 - 14$ (b) $-68.39 - 48 + 14$
(c) $68.39 - 48 + 14$ (d) $68.39 + 48 + 14$
23. The enthalpy of combustion of cyclohexane, cyclohexene and H_2 are -3920 , -3800 and -24 kJ mol^{-1} . Heat of hydrogenation of cyclohexene is
- (a) -121 kJ mol^{-1} (b) -242 kJ mol^{-1}
(c) $+121 \text{ kJ mol}^{-1}$ (d) $+242 \text{ kJ mol}^{-1}$
24. According to the Hess's law
- (a) Energy can be converted from one form to another
(b) $K_p = K_c RT^{\Delta n}$

- (c) The enthalpy change of a given chemical reaction is same whether the process occurs in one or more steps
- (d) Energy can be absorbed or released in a reaction but the total energy change of the reacting system and its surroundings remain constant
25. A hypothetical reaction $A \rightarrow 2B$ proceeds via the following sequence of steps
- (i) $A \rightarrow C$: $\Delta H = q_1$
- (ii) $C \rightarrow D$: $\Delta H = q_2$
- (iii) $\frac{1}{2} D \rightarrow B$: $\Delta H = q_3$
- The heat of reaction is
- (a) $q_1 - q_2 + q_3$ (b) $q_1 + q_2 - 2q_3$
- (c) $q_1 + q_2 + 2q_3$ (d) $q_1 + 2q_2 - 2q_3$
26. Which of the following equation represents the fundamental thermodynamic relation
- (a) $dH = TdS + VdP$ (b) $dA = -SdT - PdV$
- (c) $dG = VdP - SdT$ (d) All the above
27. For Claypeyron–Clausius equation $\log \frac{P_2}{P_1} = \dots\dots$
- (a) $\frac{\Delta H_{\text{vap}}}{R}$ (b) $\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
- (c) $\frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ (d) $\frac{-\Delta H_{\text{vap}}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
28. $\left[\frac{\partial \left(\frac{\Delta A}{T} \right)}{\partial T} \right]_V = ?$
- (a) $-\frac{\Delta E}{T^2}$ (b) $-\frac{\Delta H}{T^2}$
- (c) $\frac{\Delta E}{T^2}$ (d) $\frac{\Delta H}{T^2}$
29. Choose the correct expression
- (a) $\left(\frac{\partial S}{\partial V} \right)_T = - \left(\frac{\partial P}{\partial T} \right)_V$ (b) $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$
- (c) $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$ (d) $\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$

30. The Joule–Thomson coefficient μ_{JT} is defined by

(a) $\left(\frac{\partial T}{\partial P}\right)_S$

(b) $\left(\frac{\partial P}{\partial T}\right)_S$

(c) $\left(\frac{\partial T}{\partial P}\right)_H$

(d) $\left(\frac{\partial P}{\partial T}\right)_H$

Solution

1 (c)	2 (a)	3 (d)	4 (c)	5 (d)	6 (b)	7 (a)	8 (c)
9 (c)	10 (c)	11 (a)	12 (c)	13 (c)	14 (d)	15 (b)	16 (d)
17 (b)	18 (a)	19 (c)	20 (a)	21 (a)	22 (b)	23 (a)	24 (c)
25 (c)	26 (d)	27 (c)	28 (a)	29 (b)	30 (c)		

Chapter 16

ELECTROCHEMISTRY

16.1 Introduction

Electrochemistry is the branch of science which deals with the relationship between electrical energy and chemical energy and the inter-conversion of one form into other. If electrical energy brings about chemical reactions to occur, then the process is called electrolysis; for example, water can be made to split into hydrogen and oxygen by the passage of electric current. On the other hand, electrical energy can be produced as a result of chemical change. Both the above changes are called electrochemical changes and the latter finds use in the manufacture of cells and batteries, which generate electricity due to chemical changes. Both types of changes have widespread applications in chemistry. This chapter, however, deals only with the conversion of chemical energy into electrical energy and its applications in chemistry.

16.2 Types of Conductors

Conductors are substances which allow electricity to pass through them, for example, copper, silver and gold. Those substances which do not allow the passage of electric current through them are called non-conductors or insulators; for example, wood, rubber, etc.

Conductors can be of two types:

- (i) **Metallic conductors** Metallic conductors allow electricity to pass through them without undergoing any chemical change. The flow of electric current through metallic conductors is due to the flow of electrons in the metal. Common examples of metallic conductors are metals like copper, silver, etc.
- (ii) **Electrolytic conductors** These are substances which allow electricity to pass through them in their molten states or in their aqueous solutions. Electric current brings about decomposition in them. The charge is carried by the ions and conduction occurs due to the movement of ions. Thus, these substances do not conduct electricity in solid state but in molten state or in aqueous solutions, as the ions can move about freely in molten state or in

aqueous state. Substances like these are termed as electrolytes. Example: Molten solution of NaCl. The differences between metallic and electrolytic conductors are summarised in Table 16.1.

- (iii) **Non-electrolytes** These are substances which do not conduct electricity at all, neither in their molten state nor in their aqueous solution. Example: sugar, glucose, urea, etc.

Table 16.1 Difference between metallic and electrolytic conductors

Metallic conductors	Electrolytic conductors
1. Conduction occurs due to the movement of electrons	Conduction occurs due to the movement of ions
2. The chemical properties of the conductor do not change	The electrolyte decomposes as the result of a chemical reaction
3. It does not involve the transfer of any matter	It involves the transfer of matter in the form of ions
4. Metallic conductance decreases with the increase in temperature	Electrolytic conductance increases with the increase in temperature

16.3 Conductance in Electrolytic Solutions

When voltage is applied to electrodes dipped into an electrolytic solution and the ions of an electrolyte move, there is flow of electric current in the solution. This is termed as conductance which may be defined as the power of electrolytes to conduct electricity. Like metallic conductors, electrolytic solutions also obey Ohm's law.

Ohm's law The electric current flowing across a conductor is directly proportional to the potential difference across the conductor.

$$I \propto V$$

$$V = IR \text{ or } R = V/I \quad (1)$$

R = Proportionality constant called the resistance of the conductor in ohm (Ω)

I = Current in amperes

V = Potential difference in volts

Resistance It is the obstruction to the flow of current. It is expressed as R and its unit is ohm (Ω)

Specific resistance or resistivity: When a metallic conductor is a part of an electric circuit, the resistance R offered by it is directly proportional to the length l and inversely proportional to the area of cross section ' a ' of the conductor. It can be expressed mathematically as

$$R \propto \frac{l}{a}$$

$$R = \rho \frac{l}{a} \quad (3)$$

where ρ (rho) is a constant called the 'specific resistance or resistivity' of the conductor. Its SI unit is ohm m (Ω m) although its sub-multiple ohm cm is frequently used. IUPAC recommends the use of the term resistivity over specific resistance. An electrolytic solution shows a similar behavior. In this case, the resistance offered by the solution is the resistance of the solution enclosed between the electrodes. l represents the length of the solution, that is, the distance between the electrodes and ' a ' is the area of the smaller electrode (if they are of unequal size) exposed to the solution. In fact if we divide the volume of the solution enclosed between the electrodes by the distance between them we get the effective area of cross section of the volume of the solution.

If $l = 1$ and $a = 1$ then $\rho = R$ or resistivity of a substance in a solution is defined as the resistance offered by a meter cube or centimeter cube of the solution.

$$1 \text{ ohm m} = 100 \text{ ohm cm} \text{ or } 1 \text{ ohm cm} = 0.01 \text{ ohm m}$$

Conductance

It is the reciprocal of resistance and is a measure of the ease with which the current flows through a conductor. It is denoted by the symbol G

$$G = \frac{1}{R} \quad (3)$$

Its unit is ohm^{-1} (reciprocal ohm is also called mho represented by the symbol \mathfrak{U}). The SI units of conductance are siemens represented by the symbol S and $1S = 1\text{ohm}^{-1}$.

Specific Conductance (Conductivity)

The reciprocal of resistivity (specific resistance) is called specific conductance or conductivity and is denoted by the Greek letter kappa (κ). As per the IUPAC recommendations, the term conductivity is used over specific conductance. It is measured in $\text{ohm}^{-1}\text{cm}^{-1}$ or $S \text{ cm}^{-1}$. The SI unit of conductance is seimens, length is m and area of cross section is m^2 ; hence the SI unit of conductivity (κ) is seimens per meter ($S \text{ m}^{-1}$).

It may be noted that $1 S \text{ cm}^{-1} = 100 S \text{ m}^{-1}$

$$\begin{aligned} \therefore \rho &= R \times \frac{a}{l} \\ \frac{1}{\rho} &= \frac{l}{R \times a} \quad \text{or} \quad \kappa = \frac{l}{R \times a} \end{aligned} \quad (4)$$

Equivalent and Molar Conductivity

The conductivity of an electrolyte varies with concentration (it decreases with decrease in concentration); therefore, the conductivities of different electrolytes must be carried out at equivalent concentrations.

The equivalent conductivity of an electrolyte is the conductance of all ions produced by 1 g equivalent of an electrolyte. It is given by product of conductivity of the solution and the volume in cc containing 1 gram equivalent of the electrolyte. It is denoted by Λ (lambda). Thus if κ is the

conductivity and V the volume in cubic centimeters containing 1 g equivalent of the electrolyte, then

$$\Lambda = \kappa \times V \quad (5)$$

If the concentration of the solution is c (i.e., c gm equivalent per liter), then the volume in liters which contains one gram equivalent of the electrolyte is $1000 / c$.

Equation (5) can be written as

$$\Lambda = \kappa \times V = \frac{\kappa \times 1000}{c} \quad (6)$$

The units of equivalent conductivity are $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$. Its SI unit is $\text{S m}^2 \text{equiv}^{-1}$. Here, it is important to note that IUPAC has discontinued the use of the term equivalent conductivity and only molar conductivity is in use at present.

Molar conductivity (Λ_m): It is also used for the comparison of conductivities of different electrolytes. Molar conductivity is the conducting power of all ions produced by dissolving 1 g mole of an electrolyte in solution. It is given by the product of conductivity of the solution and the volume (V) in cc containing 1 gram mole of the electrolyte dissolved in it.

Mathematically,

$$\Lambda_m = \kappa \times V = \frac{\kappa \times 1000}{M}$$

where M is the concentration of the electrolyte in mole per liter. For a substance where equivalent and molecular weight are same its equivalent and molecular conductivities will have the same value. If we use S cm^{-1} as the units for κ and mol cm^{-3} as unit of concentration, then the units of molar conductivity will be $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$. However, if concentration is expressed in mol m^{-3} , then the unit of molar conductivity will be $\text{S m}^2 \text{mol}^{-1}$, which is also its SI unit. Both the units are used and are interrelated as

$$1 \text{ S m}^2 \text{mol}^{-1} = 10^4 \text{ S cm}^2 \text{mol}^{-1} \text{ or}$$

$$1 \text{ S cm}^2 \text{mol}^{-1} = 10^{-4} \text{ S m}^2 \text{mol}^{-1}$$

Measurement of conductivity The conductivity of an electrolytic solution can be obtained with the help of Eq. (4), if the resistance R , length l and area of cross-section a of the electrolytic conductor are known. Resistance is usually measured using a Wheatstone bridge. The solution whose conductivity is to be measured is placed in a special vessel called the conductivity cell. The cell consists of two electrodes made of platinum discs coated with finely divided platinum black and welded to a platinum wire fixed in two glass tubes. The glass tubes contain mercury and are tightly fixed in the ebonite cover of the cell so that the distance between the electrodes does not change during the experiment. Contact with the platinum discs is made by dipping the copper wires of the circuit in the mercury of the tubes (Fig. 16.1a). Since the use of direct current brings about electrolysis of the electrolyte and subsequent accumulation of the products at the electrodes, giving rise to back emf, alternating current is used and the galvanometer of the Wheatstone bridge is replaced by a headphone. The experimental set-up is shown in Figure 16.1b.

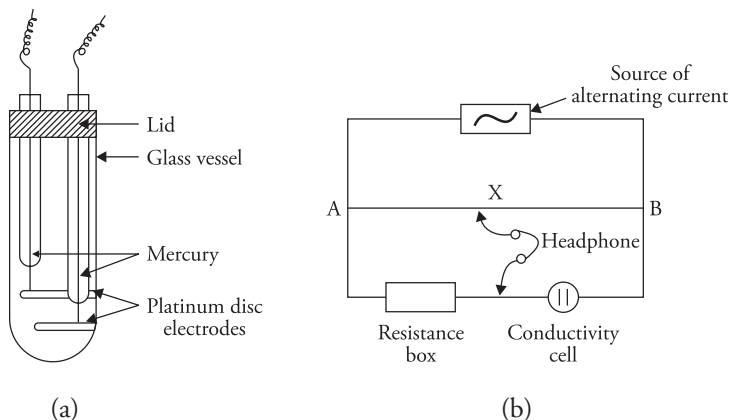


Figure 16.1 (a) Conductivity cell
(b) Experimental set-up for the measurement of conductivity of the solution of an electrolyte

AB is a wire of platinum or manganin of uniform thickness stretched along the meter bridge. The bridge is connected to a source of alternating current. R is the resistance box in one arm of the bridge. The conductivity cell is placed in the second arm of the bridge. When the apparatus is connected, a sound will be heard in the headphone. At null point, no sound will be heard or the sound will be reduced to minimum. At this point, the bridge is said to be balanced at the null point.

$$\frac{\text{Resistance of the solution in the cell}}{\text{Resistance of resistance box (R)}} = \frac{BX}{AX}$$

$$\text{Resistance of the solution} = \frac{BX}{AX} \times R$$

Resistance of the solution can be calculated from the values of AX, BX and R.

Conductivity can be obtained by multiplying the resistance with the cell constant.

Cell constant

Cell constant is the ratio of distance between the two electrodes and the area of the electrode.

$$\text{Cell constant} = \frac{\text{Distance between the electrodes}}{\text{Area of the electrodes}}$$

From Eq. (4), we have

$$\text{Conductivity } \kappa = \frac{l}{R \times a}$$

$$\text{It can be rewritten as } \kappa = \frac{\text{Cell constant}}{R}$$

Cell constant = Conductivity \times Resistance
 or, Conductivity (κ) = Conductance \times cell constant
 or, Cell constant = $\frac{\text{Conductivity}}{\text{Conductance}}$ (Since Conductance = $1/R$)

Solved examples

1. The conductivity (specific conductance) of 0.01 M KCl solution at 25 °C is $1.41 \times 10^{-3} \text{ S cm}^{-1}$. The resistance of a cell containing this solution is 8.30 ohms. What is the cell constant of the cell?

Solution

Given $R = 8.30 \Omega$ $\kappa = 1.41 \times 10^{-3} \text{ S cm}^{-1}$.

$$\begin{aligned}\text{Cell constant} &= \text{Conductivity (or specific conductance)} \times \text{Resistance} \\ &= 1.41 \times 10^{-3} \times 8.30 \\ &= 0.0117 \text{ cm}^{-1}\end{aligned}$$

2. The conductivity of 0.1 M KCl at 25 °C is $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a cell containing this solution and 0.003186 M NaCl solution are 192.3 and 6363 ohms at 25 °C. What are the specific and equivalent conductivities of NaCl at 25 °C?

Solution

$$\begin{aligned}\text{Cell constant} &= \text{Conductivity (or specific conductance)} \times \text{Resistance} \\ &= 1.29 \times 10^{-2} \times 192.3 \\ &= 2.4806 \text{ cm}^{-1}\end{aligned}$$

Specific conductivity of NaCl solution

$$= \frac{\text{Cell constant}}{\text{Resistance}} = \frac{2.4806}{6363} = 3.898 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductivity of NaCl solution

Concentration $c = 0.003186 \text{ M}$

$$\text{Equivalent conductivity} = \text{Conductivity (or specific conductance)} \times \frac{1000}{c}$$

$$= \frac{0.0003898 \times 1000}{0.003186} = 122.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

3. A conductance cell filled with 0.01 M solution of an electrolyte offered a resistance of 280 ohms. If the electrodes of the cell are 1.82 cm apart and have an area of cross-section equal to 4.64 sq cm, calculate (i) specific conductance and (ii) molar conductivity of the solution.

Solution

$$\text{Conductivity (Specific conductance)} \quad \kappa = \frac{l}{R \times a}$$

$$= \frac{1}{280} \times \frac{1.82}{4.64} = 0.001401 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Molar conductivity

$$\Lambda_m = \frac{1000 \times \kappa}{c}$$

$$\kappa = 0.001401 \text{ ohm}^{-1} \text{ cm}^{-1}; \quad c = 0.01 \text{ mol L}^{-1}$$

$$\Lambda_m = \frac{1000 \times 0.001401}{0.01} = 140.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

4. Calculate the equivalent conductivity of 1 M H_2SO_4 solution whose conductivity is $26 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$

Solution

Conductivity or specific conductance $\kappa = 26 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$

Concentration = 1 M $\text{H}_2\text{SO}_4 = 98 \text{ g/L}$

Equivalent weight of $\text{H}_2\text{SO}_4 = 49$

Gram equivalent per liter = $98/49 = 2$

$$\text{Equivalent conductivity } \Lambda = \frac{1000 \times \kappa}{c}$$

$$= \frac{26 \times 10^{-2} \times 1000}{2} = 130 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$$

5. A conductivity cell filled with 0.1 mol L^{-1} KCl solution has a resistance of 120Ω . Calculate the conductivity and molar conductivity if the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 500Ω . The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 S m^{-1} .

Solution

Cell constant = conductivity \times resistance

$$1.29 \times 120 \Omega = 154.8 \text{ m}^{-1} = 1.54 \text{ cm}^{-1}$$

$$\text{Conductivity of } 0.02 \text{ mol L}^{-1} \text{ KCl solution} = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{154.8}{500 \Omega} = 0.3096 \text{ S m}^{-1}$$

Molar conductivity $\Lambda_m = \frac{\kappa}{c}$ where c is concentration in mol m^{-3}

$$\text{Concentration} = 0.02 \text{ mol L}^{-1} = 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

$$\therefore \Lambda_m = \frac{0.3096}{20} = 0.01548 \text{ S m}^2 \text{ mol}^{-1} = 154.8 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

In CGS system:

$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{1.548 \text{ cm}^{-1}}{500 \Omega} = 3.08 \times 10^{-3} \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{c} = \frac{3.08 \times 10^{-3} \text{ S cm}^{-1} \times 1000}{0.02} = 154.8 \text{ S cm}^2 \text{ mol}^{-1}$$

6. Calculate the resistivity, conductivity and molar conductivity of a column of diameter 1 cm and length 25 cm containing NaOH solution (0.05 mol L⁻¹) having electrical resistance $2.25 \times 10^3 \text{ ohm}$.

Solution

$$a = \pi r^2 = 3.14 \times (0.5)^2 = 0.785 \text{ cm}^2$$

$$R = \rho \frac{l}{a}$$

$$\text{or } \rho = \frac{Ra}{l} = \frac{2.25 \times 10^3 \Omega \times 0.785 \text{ cm}^2}{25 \text{ cm}} = 70.65 \Omega \text{ cm} \quad \therefore \text{Resistivity} = 70.65 \Omega \text{ cm}$$

$$\text{Conductivity } \kappa = \frac{1}{\rho} = \frac{1}{70.65} = 0.01415 \text{ S cm}^{-1}$$

$$\text{Molar conductivity } \Lambda_m = \frac{\kappa \times 1000}{c} = \frac{0.01415 \text{ S cm}^{-1} \times 1000}{0.05} = 283.08 \text{ S cm}^2 \text{ mol}^{-1}$$

In SI units:

$$\text{Resistivity} = 70.65 \times 10^{-2} \Omega \text{ m}$$

$$\text{Conductivity} = 0.01415 \times 10^2 \text{ S m}^{-1}$$

$$\text{Molar conductivity} = 283.08 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

Practice problems

- The resistance of a conductance cell containing 0.1 N KCl solution at 25 °C is 456.4 ohms. The conductivity (specific conductance) of a 0.1 N KCl solution at 25 °C is 0.012886 ohm⁻¹ cm⁻¹. Calculate the cell constant. [Ans 5.881 cm⁻¹]
- The resistance of a conductance cell containing 0.1 N KCl solution at 25 °C was found to be 307.62 ohm. The conductivity (specific conductance) of 0.1 N KCl solution is known to be 0.012886 ohm⁻¹ cm⁻¹. The same cell when filled with 0.1 N AgNO₃ solution at 25 °C offered a resistance of 362.65 ohms. Calculate (i) cell constant, (ii) conductivity and (iii) equivalent conductivity of 0.1 N AgNO₃ solution.
[Ans Cell constant = 3.964 cm⁻¹; conductivity = 1.092 × 10⁻² ohm⁻¹cm⁻¹; equivalent conductivity = 109.2 ohm⁻¹cm² equiv⁻¹]

3. When a solution of an electrolyte of specific conductance $0.003328 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C was placed in a conductance cell, the resistance was found to be 314 ohms at 25°C . Calculate the cell constant. If the area of cross-section of each electrode is 1.44 sq cm , calculate the distance between the electrodes.

[Ans Cell constant = 1.045 cm^{-1} ; distance between the electrodes $l = 1.505 \text{ cm}$]

4. A conductivity cell when filled with 0.02 M KCl (conductivity = $0.002768 \text{ ohm}^{-1} \text{ cm}^{-1}$) has a resistance of 457.3 ohm . What will be the equivalent conductivity of 0.05 N CaCl_2 solution if the same cell filled with this solution has a resistance of 202 ohm ?

[Ans $125.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$]

16.4 Factors Affecting Conductance

The factors affecting conductance of an electrolytic solution are as follows.

- Nature of the electrolyte** Electrolytic conductance depends upon two factors (i) the inter-ionic forces between ions of the electrolyte and (ii) the number of ions furnished by the electrolyte. The weaker the inter-ionic forces of attraction, the greater will be the conductivity and vice versa. Moreover, some electrolytes dissociate completely in solution (strong electrolytes); their conductivity is high, for example, NaCl , KNO_3 , etc. On the other hand, some electrolytes dissociate to a lesser extent (weak electrolytes); their conductivity is low.
- Solvation of the ions** These are solute–solvent interactions. If the solute–solvent interactions are strong, the solute will be heavily solvated and the solvent molecules will hold it tightly. As a result, its electrical conductivity will be low.
- Viscosity of the solvent** A viscous solvent resists the movement of the solute particles. The mobility of ions and the conductivity of the electrolyte increases with the decrease in the viscosity of the solvent.
- Temperature** As the temperature increases, the average kinetic energy of the molecules rises. Moreover, with the rise in temperature, the viscosity of the solvent decreases. Hence, the conductivity of an electrolytic solution increases with the increase in temperature.
- Concentration / Dilution**

Variation of conductivity (specific conductance) with dilution Specific conductance (κ) is proportional to the number of ions per unit volume. As the concentration decreases or the dilution increases, the number of ions per cm^3 of the solution decreases. Although in case of weak electrolytes the degree of dissociation increases but due to the decrease in the number of ions per unit volume the specific conductance of both strong and weak electrolytes decreases on dilution.

Variation of equivalent and molar conductivity with dilution The molar conductivity of an electrolyte increases with decrease in concentration or increase in dilution. This is because the number of ions of the electrolyte (degree of dissociation) increases as the solution is diluted. Molar conductivity Λ_m is the product of specific conductance κ and volume V ($\Lambda_m = \kappa \times V$). On dilution, κ decreases and V increases. However, the rate of decrease in κ is less than the

increase in volume V , hence molar conductivity Λ_m increases with dilution. The variation of molar conductivity for strong and weak electrolytes can be studied separately.

- (i) **Variation of molar/equivalent conductivity for strong electrolytes** Strong electrolytes like KCl, NaCl and KNO_3 , are almost completely dissociated at all dilutions. Their conductivity increases only very slightly with the decrease in concentration or increase in dilution. This is because although on dilution the number of ions do not increase; the interionic interactions decrease thereby increasing the molar conductivity. At infinite dilution, the conductivity reaches its maximum value as the interionic interactions at infinite dilution are supposed to be entirely absent. Thus, the limiting value is known as equivalent or molar conductivity at infinite dilution (denoted by the symbol Λ_m^∞ or Λ_{eq}^∞). It can be obtained by extrapolation of the concentration curve of a strong electrolyte to zero concentration (Fig. 16.2a). Kohlrausch demonstrated the concentration dependence of molar conductivity for strong electrolytes

$$\Lambda_m = \Lambda_m^\infty - Ac^{1/2}$$

Hence for strong electrolytes molar conductivity decreases as a square root of concentration. At ∞ dilution when $c \rightarrow 0$, $\Lambda_m = \Lambda_m^\infty$

- (ii) **Variation of molar/equivalent conductivity for weak electrolytes** For weak electrolytes like CH_3COOH , the equivalent or molar conductivity is low but increases steadily with dilution. This is because in such compounds, the number of ions furnished in a concentrated solution is less; as concentration decrease the degree of dissociation increases. This means that on dilution the same amount of electrolyte is capable of furnishing larger number of ions. Hence as the solution is diluted, the number of ions increases and hence, the conductivity also increases. However, here a limiting value of conductivity cannot be obtained even when the concentration approaches zero and it cannot be calculated by extrapolation of curve to zero concentration (Fig. 16.2 b), and hence molar conductivity at infinite dilution for weak electrolytes is determined by Kohlrausch law discussed in the forthcoming section (Section 16.5).

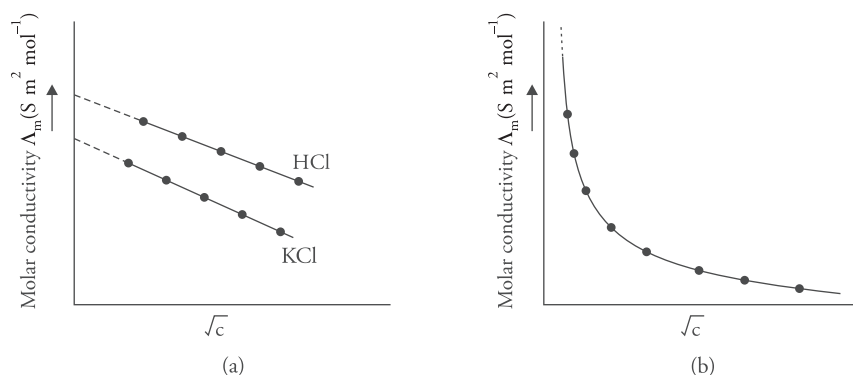


Figure 16.2 Variation of equivalent / molar conductivity with square root of concentration for (a) strong electrolytes and (b) weak electrolytes

Degree of dissociation

It is the ratio of molar/equivalent conductivity at a particular concentration to the molar/equivalent conductivity at infinite dilution.

$$\alpha = \frac{\Lambda_{eq}^c}{\Lambda_{eq}^\infty} = \frac{\text{Equivalent conductivity at a given concentration}}{\text{Equivalent conductivity at infinite dilution}}$$

$$= \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\text{Molar conductivity at a given concentration}}{\text{Molar conductivity at infinite dilution}}$$

16.5 Kohlrausch's Law of Independent Migration of Ions

While studying the conductivity of electrolytes at different concentrations, Kohlrausch observed that at infinite dilution, the difference in the conductivity was similar irrespective of the other ion present (Table 16.2).

Table 16.2 Molar conductivities at infinite dilution at 18 °C

Pairs of electrolytes with same anion	$\Lambda_m^\infty/10^{-4}$ (S m ² mol ⁻¹)	Difference / 10 ⁻⁴ (S m ² mol ⁻¹)	Pairs of electrolyte with same cation	$\Lambda_m^\infty/10^{-4}$ (S m ² mol ⁻¹)	Difference / 10 ⁻⁴ (S m ² mol ⁻¹)
KF	129.21	23.42	KCl	149.86	20.62
NaF	105.79		KF	129.21	
KCl	149.86	23.41	NaCl	126.45	20.66
NaCl	126.45		NaF	105.79	
KNO ₃	144.96	23.41	KNO ₃	144.96	27.40
NaNO ₃	121.55		KIO ₃	117.56	
KIO ₃	117.56	23.41	NaNO ₃	121.55	27.40
NaIO ₃	94.15		NaIO ₃	94.15	

On the basis of the above observation, Kohlrausch in 1876 postulated a law known as the Kohlrausch's law of independent migration of ions. It states that *at infinite dilution, every ion makes a definite contribution towards the molar/equivalent conductivity irrespective of the other ions associated with it.*

Hence, the equivalent/molar conductivity at infinite dilution is equal to the sum of the ionic conductance of the constituent ions.

If the molar conductivity of the cation is λ_+^∞ and that of the anion is λ_-^∞ , then according to Kohlrausch's law,

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

where ν_+ and ν_- are the number of cations and anions according to the formula of the electrolyte (for example, for BaCl_2 , $\nu_+ = 1$ and $\nu_- = 2$), λ_+^∞ and λ_-^∞ are the molar ionic conductivity of the positive and negative ions at infinite dilution. Table 16.3 gives the molar conductivity of some ions in water at 25 °C.

Table 16.3 Molar ionic conductivity of some ions in water at 25 °C

Cation	$\lambda_+^\infty/10^{-4} \text{ (S m}^2 \text{ mol}^{-1}\text{)}$	Anion	$\lambda_-^\infty/10^{-4} \text{ (S m}^2 \text{ mol}^{-1}\text{)}$
H^+	349.83	Cl^-	76.34
Na^+	50.11	Br^-	78.40
K^+	73.52	I^-	76.8
Li^+	38.70	OH^-	199.1
Ag^+	61.92	NO_3^-	71.4
Ca^{2+}	119.0	SO_4^{2-}	159.6
Mg^{2+}	106.0	CH_3COO^-	40.89

Applications of Kohlrausch's law

1. Calculation of equivalent/molar conductivity for weak electrolytes at infinite dilution

As discussed earlier, it is not possible to find the equivalent/molar conductivity of weak electrolytes at infinite dilution by extrapolation of the graph of molar conductivity $\nu/s \sqrt{c}$.

However, molar conductivity can be calculated using Kohlrausch's law.

To calculate the molar conductivity of CH_3COOH at infinite dilution, the molar conductivity of strong electrolytes containing H^+ and CH_3COO^- ions is determined.

$$\Lambda_m^\infty(\text{CH}_3\text{COOH}) = \lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{H}^+}^\infty \quad (1)$$

Strong electrolytes HCl , NaCl and CH_3COONa are considered.

$$\Lambda_m^\infty(\text{HCl}) = \lambda_{\text{H}^+}^\infty + \lambda_{\text{Cl}^-}^\infty \quad (2)$$

$$\Lambda_m^\infty(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{Na}^+}^\infty \quad (3)$$

$$\Lambda_m^\infty(\text{NaCl}) = \lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty \quad (4)$$

$\Lambda_m^\infty(\text{CH}_3\text{COOH})$ can be obtained from (2) + (3) – (4).

$$\Lambda_m^\infty(\text{CH}_3\text{COOH}) = \Lambda_m^\infty(\text{HCl}) + \Lambda_m^\infty(\text{CH}_3\text{COONa}) - \Lambda_m^\infty(\text{NaCl})$$

Similarly, molar conductivity of NH_4OH at infinite dilution can be determined as

$$\Lambda_m^\infty(\text{NH}_4\text{OH}) = \Lambda_m^\infty(\text{NH}_4\text{Cl}) + \Lambda_m^\infty(\text{NaOH}) - \Lambda_m^\infty(\text{NaCl})$$

2. Determination of degree of dissociation of weak electrolytes

As discussed earlier,

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

Solved examples

1. At 25 °C, the molar conductivities at infinite dilution of ammonium chloride, sodium hydroxide and sodium chloride are 149.7, 248.11 and 126.45 ohm⁻¹ cm² mol⁻¹, respectively. Calculate the molar conductivity of ammonium hydroxide at infinite dilution at 25 °C.

Solution

We know that

$$\Lambda_m^\infty(\text{NH}_4\text{OH}) = \Lambda_m^\infty(\text{NH}_4\text{Cl}) + \Lambda_m^\infty(\text{NaOH}) - \Lambda_m^\infty(\text{NaCl})$$

$$\Lambda_m^\infty(\text{NH}_4\text{Cl}) = 149.70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\infty(\text{NaOH}) = 248.11 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\infty(\text{NaCl}) = 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\infty(\text{NH}_4\text{OH}) = 149.70 + 248.11 - 126.45$$

$$= 271.36 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$= 271.36 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

2. When a cell is filled with 0.1 M KCl solution, its resistance was found to be 192.3 ohms and when the same cell is filled with 3.186 M NaCl solution, its resistance was found to be 6.306 ohms at 25 °C. Calculate (i) the cell constant, (ii) the conductivity (specific conductance) and molar conductivities of NaCl solution and (iii) the degree of dissociation of NaCl solution at this dilution (given specific conductivity of 0.1 M KCl is 0.01289 ohm⁻¹ cm⁻¹ at 25 °C). Molar conductivity of sodium and chloride ions at 25 °C are 50.11 and 76.34 ohm⁻¹ cm² mol⁻¹, respectively.

Solution

(i) Cell constant = Conductivity × Resistance

$$= 0.01289 \text{ ohm}^{-1} \text{ cm}^{-1} \times 192.3 \text{ ohm} = 2.479 \text{ cm}^{-1}$$

(ii) Conductivity of 3.186 × 10⁻³ M NaCl solution is = $\frac{\text{Cell constant}}{\text{Resistance}}$

$$\frac{2.479 \text{ cm}^{-1}}{6.306 \text{ ohm}} = 0.3931 \text{ ohm}^{-1} \text{ cm}^{-1}$$

The concentration of NaCl solution is 3.186 M

$$\Lambda_m^c = \frac{\text{Conductivity}(\kappa) \times 1000}{c}$$

$$= 0.3931 \times \frac{1000}{3.186} = 123.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\text{Now, } \Lambda_m^\infty = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 50.11 + 76.34 = 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

∴ degree of dissociation

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{123.4}{126.45} = 0.976 \text{ or } 97.6\%$$

3. The conductivity of a 0.01 M solution of acetic acid is 0.000143 mhos cm^{-1} . The limiting molar ionic conductivities of hydrogen and acetate ions at the same temperature are 349.6 and 40.9 $\text{S cm}^2 \text{ mol}^{-1}$, respectively. Calculate the degree of ionisation at this temperature.

Solution

Concentration of the solution $c = 0.01 \text{ M}$

$$\text{Now Molar conductivity } \Lambda_m^c = \frac{\text{Conductivity}(\kappa) \times 1000}{c}$$

$$\Lambda_m^c = \frac{0.000143 \times 1000}{0.01} = 14.3 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\Lambda_m^c}{\lambda_{\text{H}^+}^\infty + \lambda_{\text{CH}_3\text{COO}^-}^\infty} = \frac{14.3}{349.6 + 40.9} = 0.0366$$

Hence the degree of ionisation of acetic acid = 3.66%.

4. The conductivity of a saturated solution of silver chloride at 20 °C is $1.33 \times 10^{-6} \text{ mho cm}^{-1}$. Given that the ionic conductivities of silver and chloride ions at infinite dilution are 56.9 and 68.4 mho cm^{-1} , respectively. Calculate the solubility and solubility product of silver chloride.

Solution

Given

$$\kappa_{\text{AgCl}} = 1.33 \times 10^{-6} \text{ S cm}^{-1}$$

$$\lambda_{\text{Ag}^+}^\circ = 56.9 \text{ S cm}^{-1}$$

$$\lambda_{\text{Cl}^-}^\circ = 68.4 \text{ S cm}^{-1}$$

Solubility of AgCl = ? Solubility product of AgCl = ?

Molar conductivity of AgCl at infinite dilution

$$\Lambda_m^\circ \text{ AgCl} = \lambda_{\text{Ag}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

$$= 56.9 \text{ S cm}^{-1} + 68.4 \text{ S cm}^{-1} = 125.3 \text{ S cm}^{-1}$$

To calculate solubility

$$\Lambda_m^o \text{AgCl} = \frac{\kappa \times 1000}{c} \text{ where } c \text{ is in mol / liter}$$

$$125.3 \text{ S cm}^{-1} = \frac{1.33 \times 10^{-6} \text{ S cm}^{-1} \times 1000}{c \text{ mol/liter}}$$

$$c = \frac{1.33 \times 10^{-6} \text{ S cm}^{-1} \times 1000}{125.3 \text{ S cm}^{-1}}$$

$$c = 1.0614 \times 10^{-5} \text{ mol/liter or mol dm}^{-3}$$

$$\text{Solubility of AgCl} = 1.0614 \times 10^{-5} \text{ mol/liter or mol dm}^{-3}$$

For a binary electrolyte like AgCl

$$\text{Solubility product } K_{sp} = (\text{solubility})^2$$

$$= (1.0614 \times 10^{-5} \text{ mol dm}^{-3})^2$$

$$= 1.12 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

Practice problems

1. The molar conductivities at infinite dilution of sodium acetate, hydrochloric acid and sodium chloride are 91.0, 426.2 and 126.5 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, respectively, at 298 K. Determine the molar conductivity of acetic acid at infinite dilution. [Ans 390.7 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$]
2. The molar conductivity at infinite dilution for AgNO_3 , NaCl and NaNO_3 is 116.5, 110.3 and 105.2 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, respectively. The conductivity of AgCl in water is $2.4 \times 10^{-6} \text{ ohm}^{-1} \text{cm}^{-1}$ and of water used for the preparation of solution is $1.16 \times 10^{-6} \text{ ohm}^{-1} \text{cm}^{-1}$. Find the solubility of AgCl in g dm^{-3} . [Ans $1.4622 \times 10^{-3} \text{ g dm}^{-3}$]
3. At 18 °C, the velocity of migration of Ag^+ is 0.00057 cm per second and that of NO_3^- ions is 0.00063 cm per second. Calculate the equivalent conductivity at infinite dilution of AgNO_3 at 18 °C ($F = 96500 \text{ coulombs}$). [Ans 115.8 $\text{mho cm}^2 \text{equiv}^{-1}$]
4. The molar conductivity at infinite dilution of $\text{Al}_2(\text{SO}_4)_3$ is 858 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Calculate the molar ionic conductivity of Al^{3+} ions if $\lambda^\infty(\text{SO}_4^{2-}) = 160 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. [Ans = 189 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$]

16.6 Conductometric Titration

Conductance measurements can be used to find the end point of reactions between electrolytes, precipitation reaction, etc. These measurements are particularly useful when the electrolytes are coloured and detection of the end point by the use of an indicator is difficult.

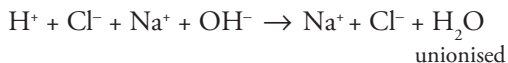
The principle involved in these titrations is based on the difference in conductance of various ions. Therefore, on gradual addition of a titrant to the titre, the conductance value changes. By plotting a graph between the volumes of titrant vs the conductance measurements, the end point of the reaction can be determined.

A brief description of different types of conductometric titrations is given below.

1. Acid–base titrations

(i) Titration of strong acid with a strong base

For such titrations, the strong acid (say HCl) is taken in the conical flask and its conductance is measured with the help of a conductivity cell. The conductance will be high as the acid contains H^+ ions which have maximum conductance. When a strong base (say NaOH) is added gradually from the burette the following ionic reaction takes place.



From the above reaction, it can be seen that the fast moving H^+ ions are replaced by slow moving Na^+ ions (as the size of Na^+ is larger than H^+ their ionic conductance is less than the ionic conductance of H^+ ions); the conductance decreases on gradual addition of the alkali. After the neutralisation is complete, further addition of alkali results in the introduction of fast moving hydroxyl ions, increasing the conductance of the solution.

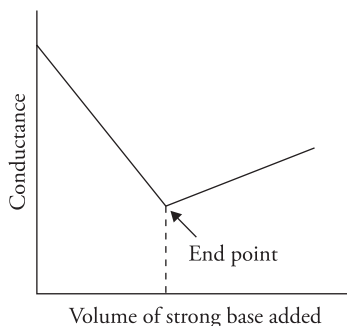
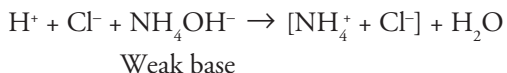


Figure 16.3 Conductometric titration: strong acid and strong base

On plotting conductance against the volume of alkali added, a graph of the type shown in Figure 16.3 is obtained. It can be seen that the graph consists of two straight lines which intersect at the equivalence point.

(ii) Titration of strong acid and weak base

If a strong acid (such as HCl) is titrated with a weak base (like NH_4OH), the conductance falls initially due to the replacement of fast moving H^+ ions by slow moving NH_4^+ ions. However, after neutralisation, the conductance will remain almost constant, since the free base is feebly ionised as it is a weak electrolyte and will not contribute much to the conductance. Therefore, the second part of the curve is almost parallel to the x -axis.



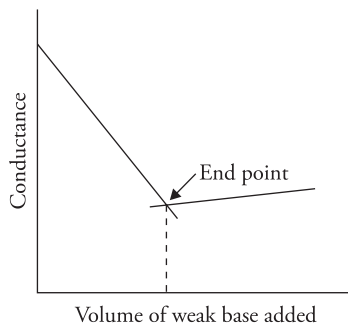


Figure 16.4 Strong acid and weak base

On plotting conductance against the volume of alkali added, a graph of the type shown in Figure 16.4 is obtained.

(iii) **Titration of weak acid and strong base**

When a weak acid like acetic acid is titrated against a strong base like sodium hydroxide, then the titration curve is obtained as shown in Figure 16.5. Although acetic acid is a weak acid, yet it furnishes some highly mobile H^+ ions which make a definite contribution to the conductance of the solution. On addition of base these H^+ ions are removed from the solution due to reaction with the base forming poorly ionised water, hence there is a slight decrease in conductance on addition of few drops of base initially. The initial decrease in conductance can also be attributed to the suppression of ionisation of acetic acid by the common acetate ions of strongly ionised sodium acetate. However, with further addition of base, the conductance of the highly ionised salt becomes greater than the conductance of the weak acid which it replaces and therefore, the conductance of the solution increases. After the neutralisation point, there is further increase in the conductance due to the presence of free base.

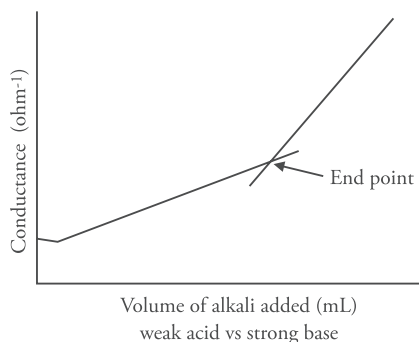
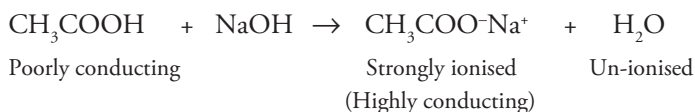
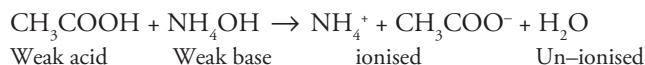


Figure 16.5 Weak acid and strong base

(iv) **Titration of a weak acid with a weak base**

Although acetic acid is a weak acid, it furnishes some highly mobile H^+ ions which make a definite contribution to the conductance of the solution. On addition of base these H^+ ions are removed from the solution due to reaction with the base ; moreover formation of ammonium acetate also suppresses the ionisation of acetic acid due to the common acetate ions (common ion effect). Both these factors lead to slight decrease in the conductance of the solution which can be seen in Figure 14.6.



Further addition of base increases the conductivity due to the formation of ionised salt ($\text{CH}_3\text{COO}^-\text{NH}_4^+$). After the neutralisation point, the conductance once again becomes constant due to free NH_4OH , which is a weak electrolyte and hence feebly ionised. On plotting conductance against the volume of alkali added, a graph of the type shown in Figure 16.6 is obtained.

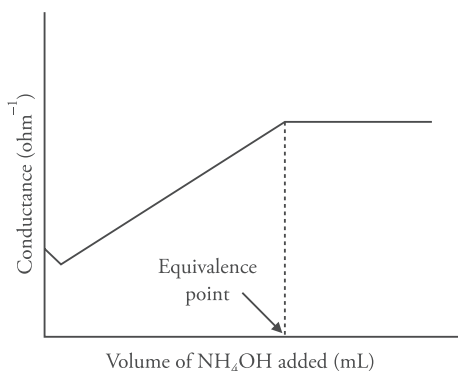
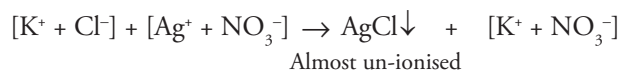


Figure 16.6 Weak acid and weak base

(v) **Precipitation titrations**

Precipitation titrations can also be followed conductometrically. Thus, when silver nitrate is added to a solution of potassium chloride, silver chloride precipitate is formed.



In the above reaction, AgCl is precipitated out and K^+ ions remain unchanged. The only change that occurs is the replacement of Cl^- ions by NO_3^- ions. Since the mobility and molar ionic conductivity of these ions is almost the same ($\lambda_{\text{Cl}^-} = 76.3$ and $\lambda_{\text{NO}_3^-} = 71.4$),

there is no change in conductivity on addition of AgNO_3 . Addition of AgNO_3 after the equivalence point brings about a sharp increase in conductance due the addition of free Ag^+ and NO_3^- ions. On plotting conductance against the volume of AgNO_3 added, a graph of the type shown in Figure 16.7 is obtained.

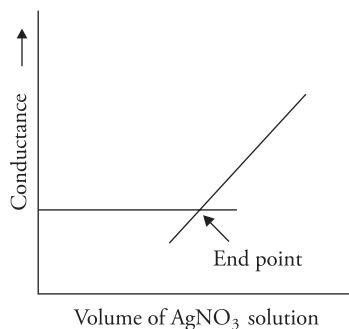


Figure 16.7 Titration of KCl solution against AgNO₃

2. Advantages of conductometric titrations

Conductometric titrations have the following advantages.

- (i) They are useful for the analysis of dilute solutions.
- (ii) They can be used for the titration of a mixture of weak acid and weak base, which do not otherwise give sharp colour changes at end points.
- (iii) Mixtures containing coloured ions can be titrated.
- (iv) Since the end point is obtained graphically, errors due to visual observation of end point (colour change) are eliminated. Hence, fairly accurate results are obtained.

16.7 Electrochemical Cell

An electrochemical cell is a device which converts chemical energy into electrical energy and vice versa. It consists of two electrodes immersed in one or more suitable electrolytes. When these electrodes are connected externally, oxidation and reduction reactions occur. The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode. Oxidation and reduction reactions occur in separate containers which are not in direct contact with each other. They are called half cells. An electrochemical cell that produces electricity as a result of chemical reactions is termed as the *galvanic cell*. An example of galvanic cell is Daniel cell. In a galvanic cell a spontaneous reaction occurring inside the cell produces electricity. An electrochemical cell in which electrical energy brings about chemical reaction is termed as the *electrolytic cell*. The reactions inside an electrolytic cell are non-spontaneous driven by an external source of current. Let us discuss a galvanic cell with the help of a typical example, the Daniel cell (Fig. 16.8). It consists of two beakers one of which contains 1.0 M solution of ZnSO₄ and the other contains 1.0 M solution of CuSO₄. A zinc rod is dipped in the ZnSO₄ solution and copper rod is dipped in the CuSO₄ solution. These metallic rods are known as electrodes. The metal rods (electrodes) are connected to an ammeter by means of an insulated wire through a key. The solutions in the two beakers are coupled by a salt bridge which is an inverted U-tube containing some electrolyte such as KCl, KNO₃ or NH₄NO₃ in a viscous medium like gelatin or agar-agar gel. These electrolytes do not undergo chemical changes during the process. The opening of the U-tube is plugged with some porous material such as glass wool or cotton.

As soon as the circuit is closed by inserting a key, current starts flowing – this is shown by deflection in the ammeter. Electric current flows due to the passage of electrons from zinc to the copper rod. The following reactions occur.

At anode $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

At cathode $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$ (Reduction)

In the external circuit, there is a flow of electrons from the zinc rod to the copper rod. Therefore, the current flows from copper to zinc. It may be noted that as a convention, the flow of electric current is taken opposite to the flow of electrons. As the electrons move from the zinc rod to the copper rod, the zinc rod is regarded as the *negative terminal*, whereas the copper rod is regarded as the *positive terminal*. The flow of the electrons occurs from the negative terminal (anode) to the positive terminal (cathode).

Thus in a galvanic cell:

Oxidation occurs at the anode (– ve terminal)

Reduction occurs at the cathode (+ ve terminal)

Electrons flow from the anode to the cathode

The two containers containing electrodes in contact with electrolyte and where the oxidation and reduction reactions occur are called half cells. The half cell where oxidation occurs is called the oxidation half cell (Zn in contact with ZnSO_4) and the half cell where reduction occurs is called the reduction half cell (Cu in contact with CuSO_4)

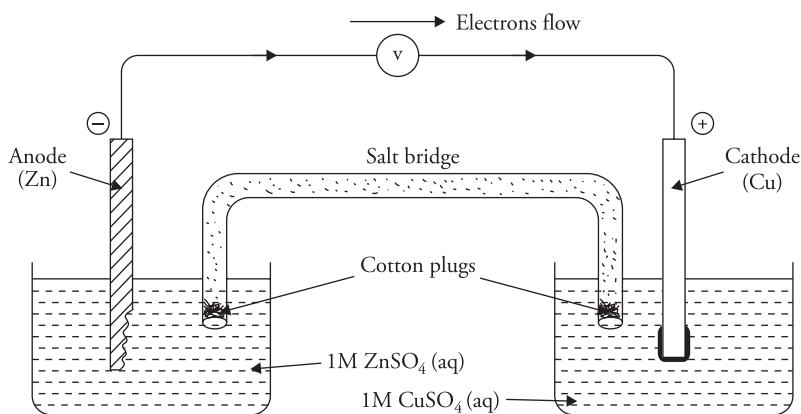


Figure 16.8 A simple galvanic cell (Daniel cell)

Functions of salt bridge

- It completes the circuit and permits ions to pass between the two half cells but does not allow Cu(II) and Zn(II) solution to pass through it thereby preventing intermixing of the solution of both the half cells.
- It prevents liquid–liquid junction potential which is harmful for the cell.

Note: For a salt bridge an electrolyte with similar mobility of anion and cation is chosen. Moreover if the cell compartments contain Ag^+ , Hg_2^{2+} or Pb^{2+} ions then KCl is not used in the salt bridge as it leads to the precipitation of AgCl , Hg_2Cl_2 and PbCl_2 .

Representation of an electrochemical cell

The following conventions are used in representing an electrochemical cell.

- (1) The anode is always written on the left and the cathode is always written on the right-hand side.
- (2) The anode of the cell is represented by writing the metal or solid phase first and then the electrolyte (or cation of the electrolyte) while the cathode is represented by writing the electrolyte first (or cation) and then, the metal or solid phase.
- (3) The metal and the cation are separated either by a vertical line (/) or by a semicolon (;)
- (4) The salt bridge which separates the two half cells is indicated by a double line (//).

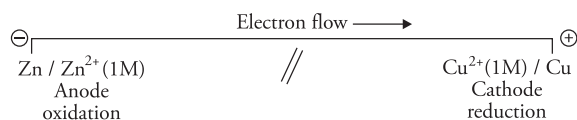
A general representation for a complete electrochemical cell is given below.

Anode (s) electrode/ anode electrolyte // cathode electrolyte / cathode(s) electrode
or Anode (s) electrode; anode electrolyte // cathode electrolyte; cathode(s) electrode

On the basis of the above convention, a Daniel cell can be represented as



Sometimes negative and positive signs are also put on the electrodes. The anode has negative polarity, as it releases electrons and the cathode has a positive polarity as it accepts electrons.



16.8 Electrode Potential and EMF of a Galvanic Cell

When a metal strip (electrode) is dipped in a solution of its own salt, for example a Zn rod is dipped in a solution of ZnSO_4 or a Cu rod is dipped in a solution of CuSO_4 then the following processes may occur (here reactions for Zn strip in a solution of ZnSO_4 are described and similar reactions will occur for Cu strip in contact with CuSO_4 solution).

- The Zn strip loses electrons



The Zn^{2+} ions will go into the solution and the electrons will remain on the Zn strip. In such a case, the zinc strip acquires a negative charge with respect to the solution.

- The Zn^{2+} ions in solution acquire electrons from the Zn strip.



In this case, solid Zn will deposit on the strip and since electrons have been taken from the metal strip it acquires a net positive charge with respect to the solution. Practically both these reactions occur simultaneously and a dynamic equilibrium exists but the rate of the two reactions is not equal. If the rate of reaction (i) is greater than the rate of reaction (ii) the metal has a greater tendency to lose electrons and get oxidized and in this case the metal strip acquires a negative charge with respect to the solution. If reaction (ii) dominates the metal strip acquires a net positive charge with respect to the solution. If the metal strip develops a negative charge then it attracts the positively charged ions in solution towards itself and vice versa (Fig. 16.9 a and b). Hence a layer of positive ions or negative ions remains close to the metal. This layer is called the Helmholtz electric double layer. Due to the above phenomenon there is separation of charges and a potential difference is set up between the metal and its solution. This potential difference between an aqueous solution of its ions and the element is termed as the *electrode potential*.

If the metal has a greater tendency to lose electrons and get oxidized it is termed as the *oxidation potential* (like in case of Zn metal in contact with ZnSO_4 solution) and if its ions have a greater tendency to accept electrons and get reduced then it is termed as the *reduction potential* (like in case of Cu metal in contact with CuSO_4 solution).

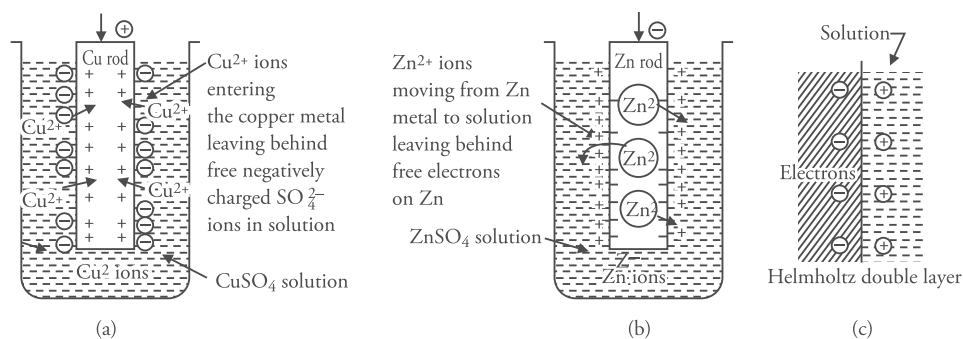


Figure 16.9 (a) Electrode becomes positive with respect to the solution (reduction)
(b) Electrode becomes negative with respect to the solution (oxidation)

The electrode potential depends upon

- Nature of metal and its ions
- Concentration of the ions in the solution and
- Temperature

According to the present convention, the half cell potentials are always represented as reduction potentials.

EMF or cell potential of a cell

An electrochemical cell is obtained by coupling two half cells or electrodes. The electrodes in these half cells have different reduction potentials. Therefore, their tendency to accept electrons is different. The electrode with higher value of reduction potential has a greater tendency to gain electrons, and behaves as a cathode. It acquires electrons from the electrode with lower reduction

potential, thereby, forcing it to undergo oxidation and behave as an anode. This difference of electrode potential between the two electrodes constituting an electrochemical cell is known as the electromotive force (EMF) or cell potential and is the driving force for the cell reaction. The potential difference is expressed in volts.

Therefore, the EMF or cell potential arises from the difference in the tendency of the two ions to get reduced. It is expressed as

$$\text{EMF} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

$$\text{or, } E_{\text{cell}} = E_{(\text{cathode})} - E_{(\text{anode})}$$

∴ Cathode is always written on the right-hand side and anode on the left-hand side, EMF of a cell may also be written as

$$E_{\text{cell}} = E_{(\text{right})} - E_{(\text{left})}$$

It is important to note that a cell reaction will be feasible only if the value of the E_{cell} is positive. A positive value of E_{cell} means that the reaction is thermodynamically favourable and ΔG will be negative making the reaction spontaneous. If the value comes out to be negative, the cell reaction is not possible and the electrodes will have to be reversed in order to bring about the cell reaction.

The cell potential or EMF of a cell can be measured with the help of a potentiometer.

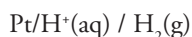
Note: Cell potential was earlier called electromotive force. This term is still widely used; however, IUPAC recommends the term cell potential over electromotive force (emf).

16.9 Measurement of Electrode Potential

It is impossible to determine the electrode potential of a single electrode (i.e., an electrode in contact with its own salt solution). The electrode potential of an electrode can be determined by combining it with other electrode called the reference electrode to form a complete cell. A *reference electrode* is an electrode of standard potential with which we can compare the potentials of other electrodes. Its potential is constant and does not depend on the analyte. Standard hydrogen electrode (SHE) is the most commonly used reference electrode. The other reference electrodes are calomel electrode, silver–silver chloride electrode, etc.

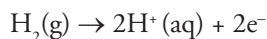
Standard Hydrogen Electrode

It is a redox electrode which is widely used as a reference electrode. It can be used either as an anode or a cathode depending upon the other electrode in the half cell. The standard hydrogen electrode consists of a platinum wire sealed in a glass tube and has a platinum foil attached to it. It is dipped into an acid solution with H^+ ions of 1 M concentration (1 M HCl). Pure hydrogen gas at 1 atmospheric pressure is constantly bubbled into the solution at a temperature of 298 K (Fig. 16.10). The reaction occurs at the surface of the foil. The electrode is denoted as

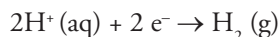


The following reaction occurs depending on whether the electrode acts as an anode or as a cathode.

If SHE acts as an anode,



If SHE acts as a cathode,



The electrode potential of an electrode is determined by connecting the half cell with a standard hydrogen electrode. The electrode potential of the standard hydrogen electrode is taken as zero. The EMF of the cell gives the value of the electrode potential of the given electrode.

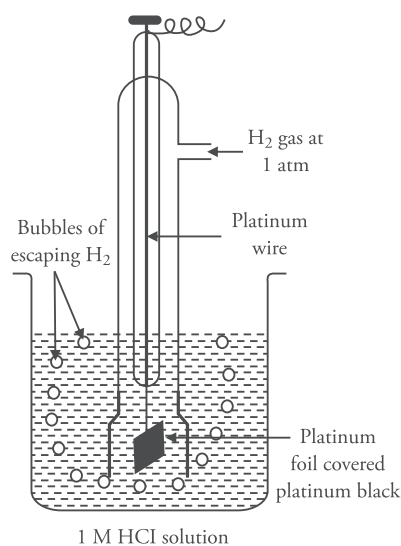


Figure 16.10 Standard hydrogen electrode

However, there are certain limitations in a hydrogen electrode. It is difficult to maintain the pressure of hydrogen gas at 1 atmosphere. Moreover, the electrode is readily affected by the compounds of Hg, As, S and oxidizing agents like Fe^{3+} , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, etc. Other reference electrodes commonly in use are discussed in Section 16.13.

16.10 Electrochemical Series

The arrangement of elements in the order of increasing reduction potential values is called electrochemical series. It is also called the activity series.

The electrochemical series of some typical electrodes with their electrode potentials is tabulated in Table 16.4.

Table 16.4 Standard reduction electrode potential at 25 °C

Electrode	Electrode reaction (reduction)	E° volts
Li ⁺ ; Li	Li ⁺ (aq) + e ⁻ → Li(s)	-3.05
K ⁺ ; K	K ⁺ (aq) + e ⁻ → K(s)	-2.93
Ba ²⁺ ; Ba	Ba ²⁺ (aq) + 2e ⁻ → Ba(s)	-2.90
Ca ²⁺ ; Ca	Ca ²⁺ (aq) + 2e ⁻ → Ca(s)	-2.87
Na ⁺ ; Na	Na ⁺ (aq) + e ⁻ → Na(s)	-2.71
Mg ²⁺ ; Mg	Mg ²⁺ (aq) + 2e ⁻ → Mg(s)	-2.37
Al ³⁺ ; Al	Al ³⁺ (aq) + 3e ⁻ → Al(s)	-1.66
Zn ²⁺ ; Zn	Zn ²⁺ (aq) + 2e ⁻ → Zn(s)	-0.76
Cr ³⁺ ; Cr	Cr ³⁺ (aq) + 3e ⁻ → Cr (s)	-0.74
Fe ²⁺ ; Fe	Fe ²⁺ (aq) + 2e ⁻ → Fe(s)	-0.44
Cd ²⁺ ; Cd	Cd ²⁺ (aq) + 2e ⁻ → Cd(s)	-0.40
Co ²⁺ ; Co	Co ²⁺ (aq) + 2e ⁻ → Co(s)	-0.28
Ni ²⁺ ; Ni	Ni ²⁺ (aq) + 2e ⁻ → Ni(s)	-0.25
Sn ²⁺ ; Sn	Sn ²⁺ (aq) + 2e ⁻ → Sn(s)	-0.14
Pb ²⁺ ; Pb	Pb ²⁺ (aq) + 2e ⁻ → Pb(s)	-0.13
2H ⁺ ; H ₂ (g); Pt	2H ⁺ (aq) + 2e ⁻ → H ₂ (g)	0.00
Cu ²⁺ ; Cu	Cu ²⁺ (aq) + 2e ⁻ → Cu(s)	+0.34
I ₂ (s); 2I ⁻ ; Pt	I ₂ (s) + 2e ⁻ → 2I ⁻ (aq)	+0.54
Fe ³⁺ ; Fe ²⁺ ; Pt	Fe ³⁺ (aq) + e ⁻ → Fe ²⁺ (aq)	+0.77
Hg ₂ ²⁺ ; Hg	Hg ₂ ²⁺ (aq) + 2e ⁻ → Hg(l)	+0.79
Ag ⁺ ; Ag	Ag ⁺ (aq) + e ⁻ → Ag(s)	+0.80
Br ₂ (l); 2Br ⁻ ; Pt	Br ₂ (l) + 2e ⁻ → 2Br ⁻ (aq)	+1.08
Cl ₂ (g); 2Cl ⁻ ; Pt	Cl ₂ (g) + 2e ⁻ → 2Cl ⁻ (aq)	+1.36
Au ³⁺ ; Au	Au ³⁺ (aq) + 3e ⁻ → Au(s)	+1.42
Mn ²⁺ ; MnO ₄ ⁻ ; Pt	MnO ₄ ⁻ (aq) + 8H ₃ O ⁺ (aq) + 5e ⁻ → Mn ²⁺ (aq) + 12H ₂ O(l)	+1.51
F ₂ (g); 2F ⁻ ; Pt	F ₂ (g) + 2e ⁻ → 2F ⁻ (aq)	+2.87

By convention standard electrode potentials are written with oxidized species on the left and reduced species on the right.

Applications of the electrochemical series

1. Relative strength of the oxidizing and reducing agents

The electrochemical series helps in predicting the oxidizing and reducing ability of a substance. In the electrochemical series, the elements are arranged in the order of their increasing reduction potential; hence, the elements situated at the bottom of the series have a greater tendency to get reduced—they are good oxidizing agents. On the other hand, elements at the top of the table have low reduction potential and have a lesser tendency of getting reduced. Consequently, they may get oxidized and are good reducing agents.

2. Calculation of cell potential or EMF of the cell

Cell potential of the cell is the difference of the reduction potential of the cathode and the anode.

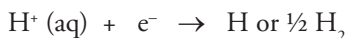
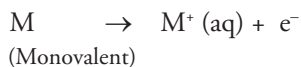
$$E^\circ_{\text{cell}} = E^\circ_{(\text{cathode})} - E^\circ_{(\text{anode})}$$

3. Predicting spontaneity or feasibility of a reaction

For a cell reaction to be spontaneous, the EMF of the cell as calculated above should be positive. If E°_{cell} is negative, then the cell reaction will not be feasible.

4. To predict whether a metal will react with acids to give H_2 gas

Those metals whose reduction potential is less than the reduction potential of hydrogen can liberate H_2 gas. Such metals are placed above hydrogen in the electrochemical series. Hydrogen having higher reduction potential has a greater tendency to accept electrons and get reduced.



Metals placed below hydrogen in the electrochemical series have a higher value of reduction potential than hydrogen. Consequently, such metals do not liberate hydrogen on reacting with acids.

5. **Replacement tendency** The metal on the top of the electrochemical series has the tendency to replace the one below it from its solution. This is because the metal placed at the bottom has a greater reduction potential and hence a greater tendency to accept electrons. For example, the standard electrode potential of Cu and Zn are as follows.

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ volts} \quad \text{and} \quad E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ volts}$$

∴ The reduction potential of copper is greater than Zn; hence, Cu^{2+} ions have a greater tendency to accept electrons.

Solved examples

1. Calculate the standard EMF of a cell containing $\text{Sn}^{2+} / \text{Sn}$ and $\text{Br}_2 / \text{Br}^-$ electrodes.

$$[E^\circ(\text{Sn}^{2+}/\text{Sn}) = -0.14 \text{ V}, E^\circ(\text{Br}_2/\text{Br}^-) = 1.08 \text{ V}]$$

Solution

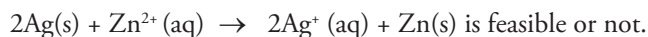
$$E^\circ_{\text{cell}} = E^\circ_{(\text{cathode})} - E^\circ_{(\text{anode})}$$

∴ Reduction potential of $E^\circ_{\text{Br}_2 / \text{Br}^-}$ is higher, it is cathodic

$$E^\circ_{\text{cell}} = E^\circ_{\text{Br}_2 / \text{Br}^-} - E^\circ_{\text{Sn}^{2+}/\text{Sn}}$$

$$= 1.08 - (-0.14) = 1.22 \text{ V}$$

2. Predict whether the reaction



Solution

From the electrochemical series, the reduction potential of Ag and Zn are as follows–

$$E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$$

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{ V}$$

According to the question, Zn^{2+} is getting reduced, hence it is behaving as a cathode.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{(\text{cathode})} - E^\circ_{(\text{anode})} \\ &= (-0.763) - (0.8) = -1.563 \text{ V} \end{aligned}$$

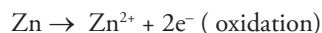
Since E°_{cell} is negative, the above reaction is not feasible or spontaneous.

3. Using the electrochemical series, predict whether zinc and silver would react with dil. H_2SO_4 or not.

Solution

The reaction of Zn with dilute H_2SO_4 can be represented as $\text{Zn} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{ZnSO}_4 + \text{H}_2(\text{g})$

The two half cell reactions are



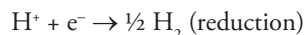
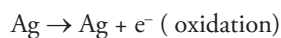
The galvanic cell can be written as



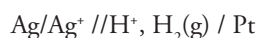
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{(\text{cathode})} - E^\circ_{(\text{anode})} \\ &= 0 - (-0.763) = +0.763 \text{ V} \end{aligned}$$

Since E°_{cell} is positive, the reaction is feasible.

Now consider the reaction of Ag with dilute H_2SO_4



The cell will be



$$E^{\circ}_{\text{cell}} = E^{\circ}_{(\text{cathode})} - E^{\circ}_{(\text{anode})}$$

$$= 0 - (0.80\text{V}) = -0.80\text{ V}$$

Since E°_{cell} is negative, the reaction is not feasible.

4. An iron wire is immersed in a solution containing ZnSO_4 and NiSO_4 . The concentration of each salt is 1 M. Predict, giving reasons, which of the following reaction is likely to proceed.

(i) Iron reduces Zn^{2+} ions (ii) Iron reduces Ni^{2+} ions,

$$\text{Given: } E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})} = -0.76\text{V}; \quad E^{\circ}_{(\text{Fe}^{3+}/\text{Fe})} = -0.44\text{ V}; \quad E^{\circ}_{(\text{Ni}^{2+}/\text{Ni})} = -0.25\text{ V}$$

Solution

(i) Since Zn^{2+} is reduced, it is cathodic and iron is anodic. Therefore,

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{(\text{Zn}^{2+}/\text{Zn})} - E^{\circ}_{(\text{Fe}^{3+}/\text{Fe})} \\ &= -0.76 - (-0.44) = -0.32\text{ V} \end{aligned}$$

Since E°_{cell} is negative, the reaction is not feasible.

(ii) Ni^{2+} is cathodic and Fe is anodic

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{(\text{Ni}^{2+}/\text{Ni})} - E^{\circ}_{(\text{Fe}^{3+}/\text{Fe})} \\ &= -0.25 - (-0.44) = +0.19\text{ V} \end{aligned}$$

Since E°_{cell} is positive, the reaction is feasible. Hence, Fe reduces Ni^{2+} .

Practice problems

1. Can a solution of 1 M CuSO_4 be stored in a vessel made of nickel metal? Given

$$E^{\circ}_{(\text{Ni}^{2+}/\text{Ni})} = -0.25\text{ V} \quad \text{and} \quad E^{\circ}_{(\text{Cu}^{2+}/\text{Cu})} = 0.34\text{ V} \quad [\text{Ans} \quad \text{No}]$$

2. Calculate E°_{cell} when the following half cell reactions are combined.



[Ans 0.72 V]

3. Calculate the standard reduction potential of Ag^{+}/Ag electrode when the cell potential for the cell.

$$\text{Cu (s)} / \text{Cu}^{2+} (1\text{ M}) // \text{Ag}^{+} (1\text{ M}) / \text{Ag} \text{ is } 0.46\text{ V. Given that } \text{Cu}^{2+} / \text{Cu} = 0.34\text{ V} [\text{Ans } 0.80\text{ V}]$$

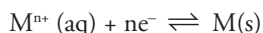
16.11 Nernst Equation

The electrode potential of an electrode depends upon the concentration of the electrolyte solution and the temperature. The electrode potential is termed as the standard electrode potential when

- Concentration of electrolyte is 1 M
- Temperature = 298 K
- Pressure of gaseous component is 1 atm or 1 bar (1.00×10^5 Pa)
- Solid components are in their standard states

Nernst equation gives the relationship between the electrode potential and the concentration of the electrolyte solutions.

Consider a general electrode reaction.



For a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are related by the Van't Hoff reaction isotherm as

$$\begin{aligned}\Delta G &= RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}\end{aligned}\quad (1)$$

ΔG^0 is the standard free energy change (i.e., the change in free energy when the concentration of the reactants and products are unity), R is the gas constant and T is the temperature.

The electrical energy is produced at the expense of the decrease in free energy, that is,

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^0 = -nFE^0$$

where n is the number of electrons liberated at one electrode, F = Faraday's constant ($1F = 96500$ coulomb)

E is the electrode potential and E^0 is the standard electrode potential.

Substituting these values in Equation (1), we have

$$\begin{aligned}-nFE &= -nFE^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{or} \\ E &= E^0 - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ E &= E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]}\end{aligned}\quad (2)$$

Since electrode reaction is always represented by reduction reaction; hence, we can write Nernst equation as

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[\text{Reduced form}]}{[\text{Oxidised form}]}$$

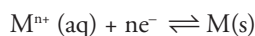
Equation (2) is called the Nernst equation and gives the dependence of electrode potential on the concentration of the electrolyte.

At $T = 298 \text{ K}$, $F = 96500$, $R = 8.314 \text{ J K}^{-1}$, Eq. (2) reduces to

$$E = E^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

For the electrode reaction



The equation becomes

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[M(\text{s})]}{[M^{n+}(\text{aq})]}$$

For pure solids, $[M(\text{s})] = 1$, and the equation becomes

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}(\text{aq})]}$$

$$= E^\circ + \frac{0.0591}{n} \log [M^{n+}(\text{aq})]$$

For a cell reaction,



The Nernst equation can be written as

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

It is evident from the Nernst equation that the electrode potential decreases with rise in temperature.

Applications of Nernst equation

1. **Calculation of cell potential of the cell** Nernst equation is used to calculate the cell potential at given electrolyte concentration

Solved examples

Q1. Calculate the potential for each half cell and the total EMF at 25 °C for the cell represented schematically as



$$E_{\text{Pb}^{2+}/\text{Pb}}^0 = -0.126 \text{ V}; \quad E_{\text{Cl}_2/2\text{Cl}^-}^0 = +1.358 \text{ V}$$

Solution

The half cell reaction at anode is



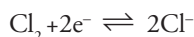
$$E_{\text{Pb}^{2+}/\text{Pb}} = E_{\text{Pb}^{2+}/\text{Pb}}^0 - \frac{0.05916}{n} \log \frac{[\text{Pb(s)}]}{[\text{Pb}^{2+}]}$$

$$= -0.126 - \frac{0.05916}{2} \log \frac{1}{0.001}$$

$$= -0.126 - \frac{0.05916 \times 3}{2}$$

$$= -0.126 - 0.09 = -0.216 \text{ V}$$

Similarly, the half cell reaction at the cathode is



$$E_{\text{Cl}_2/2\text{Cl}^-} = E_{\text{Cl}_2/2\text{Cl}^-}^0 - \frac{0.05916}{2} \log \frac{[\text{Cl}^-]^2}{[\text{Cl}_2(\text{g})]}$$

$$= -1.358 - \frac{0.05916}{2} \log(0.1)^2 \quad (\because P_{\text{Cl}_2} = 1 \text{ atm})$$

$$1.358 + 0.06 = 1.418 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 1.418 - (-0.216)$$

$$= 1.634 \text{ V}$$

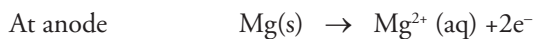
Q2. Write the Nernst equation and calculate the EMF of the following cell at 298 K.



$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34 \text{ V}; \quad E_{\text{Mg}^{2+}/\text{Mg}}^0 = -2.37 \text{ V}$$

Solution

The reactions involved are



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= 0.34 - (-2.37) = 2.71 \text{ V}$$

Substituting the values,

$$E_{\text{cell}} = 2.71 - \frac{0.0591}{n} \log \frac{0.001}{0.0001}$$

$$E_{\text{cell}} = 2.71 - 0.0295 = 2.6805 \text{ V}$$

2. Calculation of equilibrium constant

Nernst equation can be used to find the equilibrium constant of a given cell.

Consider the equilibrium reaction given below.



$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

K_c is the equilibrium constant.

The Nernst equation can be written as

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

At equilibrium, $E_{\text{cell}} = 0$; hence

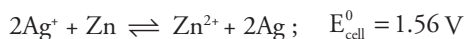
$$0 = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

$$\text{or } \log K_c = \frac{nE_{\text{cell}}^0}{0.0591} \text{ at } T = 298 \text{ K}$$

- Q3. Calculate the equilibrium constant for the reaction between silver nitrate and metallic zinc. The standard electrode potential of the cell is 1.56 V.

Solution

The cell reaction involved is



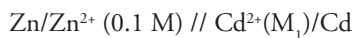
According to the Nernst equation,

$$\log K = \frac{nE_{\text{cell}}^0}{0.0591}$$

n for the above reaction is 2; hence

$$\log K = \frac{2 \times 1.56}{0.0591} = 6.192 \times 10^2$$

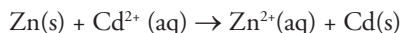
3. **To find the concentration of one ionic species in a cell if the concentration of the other species is known**
- Q4. Find the concentration of Cd^{2+} ions in the given electrochemical cell:



$$\text{Given: } E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}; E_{\text{Cd}^{2+}/\text{Cd}}^0 = -0.40 \text{ V}; E_{\text{cell}} = 0.3305 \text{ V at } 298 \text{ K}$$

Solution

The cell reaction for the above cell is



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cd}^{2+}(\text{aq})]}$$

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$= -0.40 - (-0.76) = 0.36 \text{ V}$$

Substituting this value in the Nernst equation,

$$0.3305 = 0.36 - \frac{0.0591}{2} \log \frac{0.1}{M_1}$$

$$-0.0295 = -0.0295 \log \frac{0.1}{M_1}$$

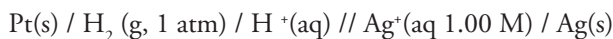
$$\log \frac{0.1}{M_1} = 1 \quad ; \quad \frac{0.1}{M_1} = 1 \text{ anti log}$$

$$\frac{0.1}{M_1} = 10 \quad \text{or} \quad M_1 = 0.01$$

4. To find the pH of a solution

Nernst equation can be used to find the pH of a solution

Q5 An electrochemical cell is represented as follows



Given $E = 0.900 \text{ V}$ at 25°C ; $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$

Find the pH of the solution.

Solution

The reactions involved are



According to Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \log \frac{[\text{H}^+]^2}{[\text{Ag}^+]^2}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.80 - (-0) = 0.80 \text{ V}$$

Substituting this value in the Nernst equation, we have

$$0.90 = 0.80 - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{[1 \text{ M}]^2}$$

$$-0.0295 \log[\text{H}^+]^2 = 0.90 - 0.80$$

$$-\log[\text{H}^+]^2 = \frac{0.100}{0.0295} = 3.3898$$

$$-2 \log[\text{H}^+] = 3.3898 \quad \text{or} \quad -\log[\text{H}^+] = 1.6949$$

$$\therefore -\log[\text{H}^+] = \text{pH}$$

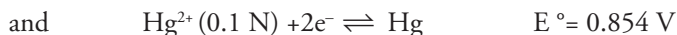
Hence,

$$\text{pH} = 1.6949$$

Practice problems

1. Calculate the oxidation potential of zinc electrode when a zinc rod is immersed in a solution of zinc sulphate in which the concentration of Zn^{2+} ions is 0.15. The standard electrode potential of zinc is 0.7618 V. [Ans 0.7681 volts]

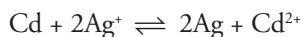
2. Represent schematically a cell made up of the following half cell reactions at 25 °C.



Calculate the cell potential of the above cell. [Ans 1.104 V]

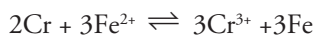
3. A zinc rod is dipped in a 0.1 M solution of ZnSO_4 . The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential if $E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$. [Ans -0.79 V]

4. Calculate the equilibrium constant for the reaction at 25 °C.



$$\text{If } E^\circ_{(\text{Cd}^{2+}/\text{Cd})} = -0.402 \text{ V}; E^\circ_{(\text{Ag}^+/\text{Ag})} = +0.80 \text{ V} \quad [\text{Ans } 4.751 \times 10^{40}]$$

5. Calculate the equilibrium constant for the reaction at 25 °C.



$$E^\circ_{(\text{Cr}^{3+}/\text{Cr})} = -0.71 \text{ V}; E^\circ_{(\text{Fe}^{2+}/\text{Fe})} = -0.44 \text{ V}$$

Calculate the equilibrium constant for the above cell reaction. [Ans 2.577×10^{27}]

6. For what concentration of $\text{Ag}^+(\text{aq})$ will the EMF of the cell be zero at 25 °C if the concentration of $\text{Cu}^{2+}(\text{aq})$ is 0.01 M.



$$\text{Given } E^\circ_{(\text{Ag}^+/\text{Ag})} = +0.80 \text{ V}; E^\circ_{(\text{Cu}^{2+}/\text{Cu})} = 0.338 \text{ V} \quad [\text{Ans } 1.477 \times 10^{-9}]$$

16.12 Thermodynamic Functions and Electrochemical Cells

Thermodynamic properties such as Gibbs free energy, enthalpy and entropy can be calculated from cell potential measurements.

Gibbs free energy and EMF of a cell

In an electrochemical cell, chemical energy is converted into electrical energy and vice versa. As we know, ΔG of a reaction is the measure of the maximum useful work that can be obtained from a chemical reaction. Hence,

$$\Delta G = \text{maximum work}$$

For a cell whose electrodes differ in potential by E_{cell} , the work done when charge nF is pushed along by the potential of the cell is given by nFE_{cell} so that

$$\text{Maximum work} = nFE_{\text{cell}}$$

F is the Faraday constant and n is the number of electrons transferred.

It was pointed out by Gibbs and independently, by Helmholtz that the electrical energy of a cell is given by the decrease in free energy ($-\Delta G$). Hence,

$$\Delta G = w_{\text{max}} = -nFE_{\text{cell}}$$

If the substances involved are in their standard states, that is, concentration of the electrolyte is 1 M, pressure is one atmosphere and temperature is 298 K then $\Delta G^0 = -nFE^0$

when $\Delta G = -ve$; or $\Delta E = +ve$, the reaction is spontaneous

$\Delta G = +ve$, $\Delta E = -ve$, the reaction is non-spontaneous

$\Delta G = 0$; or $\Delta E = 0$, the reaction is at equilibrium.

Enthalpy and EMF of cell

The enthalpy of a reaction is given by

$$\Delta H = \Delta G + T\Delta S$$

According to the Gibbs–Helmholtz equation, decrease in free energy $-\Delta G$ of the cell reaction at constant pressure would be given by the expression

$$-\Delta G = -\Delta H - T \left(\frac{\partial(\Delta G)}{\partial T} \right)_p$$

As, $-\Delta G = nFE$ or $\Delta G = -nFE$

$$nFE = -\Delta H - T \left(\frac{\partial(-nFE)}{\partial T} \right)_p$$

$$nFE = -\Delta H + nFT \left(\frac{\partial E}{\partial T} \right)_p$$

$$\text{or } E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$$

n and F are constants and $\left(\frac{\partial E}{\partial T}\right)_p$ is the temperature coefficient of the cell.

- If $\left(\frac{\partial E}{\partial T}\right)_p$ is zero, the electrical energy is equal to the enthalpy of the cell reaction.
- A positive value of temperature coefficient indicates that the cell potential (EMF) of a cell increases with rise in temperature. The electrical energy will be greater than the enthalpy of the reaction. The cell takes energy from the surroundings or its temperature falls during working.
- If the temperature coefficient is negative, the electrical energy will be smaller than the enthalpy of the reaction. The cell either losses heat to the surroundings or its temperature rises during working.

Entropy and EMF of a cell

$$\Delta G = \Delta H - T\Delta S \quad \text{and} \quad \Delta G = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$\text{Hence, } \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$

ΔS can be calculated using the above equation.

Solved examples

1. The cell potential (EMF) of a cell which is independent of the concentration of the KCl solution

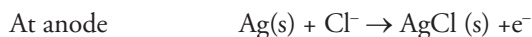


is +0.0455 volts at 25 °C and the temperature coefficient is $+3.38 \times 10^{-4}$ volts per degree. What is the reaction taking place in the cell and what are the free energy, enthalpy and entropy changes at 25 °C?

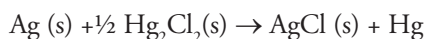
Solution

Since the EMF of the cell is positive, oxidation takes place at the left-hand electrode and reduction occurs at the right-hand electrode.

The reactions are



The overall cell reaction is



For this cell, $E = +0.0455$ volts

$$\left(\frac{\partial E}{\partial T}\right)_p = +3.38 \times 10^{-4} \text{ volts per degree}$$

$$n = 1; \quad F = 96500; \quad T = 273 + 25 = 298$$

(i) Calculation of ΔG

$$\begin{aligned} \Delta G &= -nFE \\ &= -1 \times 96500 \times 0.0455 \text{ volts coulomb} \quad (1 \text{ volt coulomb} = 1 \text{ joule}) \\ &= \frac{96500 \times 0.0455}{4.184} \text{ calories} \quad (\because 1 \text{ cal} = 4.184 \text{ volt coulomb}) \\ &= -1049.41 \text{ calories} \end{aligned}$$

(ii) Calculation of ΔH

$$\begin{aligned} E &= -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T}\right)_p \\ 0.0455 &= -\frac{\Delta H}{1 \times 96500} + 298 \times 3.38 \times 10^{-4} \\ \Delta H &= (298 \times 3.38 \times 10^{-4} - 0.0455) \times 96500 \\ &= 5329.116 \text{ volt coulomb deg}^{-1} \\ &= \frac{5329.116}{4.184} \text{ calories} = 1273.69 \text{ calories} \end{aligned}$$

(iii) Calculation of ΔS

$$\begin{aligned} \Delta S &= nF \left(\frac{\partial E}{\partial T}\right)_p \\ &= 1 \times 96500 \times 3.38 \times 10^{-4} \text{ volt coulomb deg}^{-1} \\ &= \frac{1 \times 96500 \times 3.38 \times 10^{-4}}{4.184} = 7.796 \text{ calories deg}^{-1} \end{aligned}$$

2. For a Weston cell, EMF is 1.018 V at 293 K. Its temperature coefficient $\left(\frac{\partial E}{\partial T}\right)_p = -4.00 \times 10^{-5} \text{ V K}^{-1}$. Calculate ΔG , ΔS and ΔH for the cell reaction of cell.

Solution

$$-\Delta G = nFE$$

$$= -2 \times 96500 \times 1.018 \text{ V}$$

$$= -1.964 \times 10^5 \text{ J}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p$$

$$= 2 \times 96500 \times (-4.00 \times 10^{-5} \text{ V K}^{-1})$$

$$= -7.72 \text{ J K}^{-1}$$

$$\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_p$$

$$= -2 \times 96500 \text{ C} \times 1.018 \text{ V} + [293 \text{ K} \times 2 \times 96500 \text{ C} \times (-4.00 \times 10^{-5} \text{ V K}^{-1})]$$

$$= -1.99 \times 10^5 \text{ J}$$

Practice problems

1. Consider the cell



The EMF of the cell at 15 °C is 0.67531 V and the temperature coefficient is 0.00065 V deg⁻¹. Calculate the value of ΔG , ΔS and ΔH , if the process is carried out reversibly

$$[\text{Ans } \Delta G = -130.335 \text{ kJ}; \Delta S = 125.45 \text{ J K}^{-1}; \Delta H = -94.2054 \text{ kJ}]$$

2. The voltage of the cell

$\text{Pb} / \text{PbSO}_4 / \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} / \text{Hg}_2\text{SO}_4 / \text{Hg}$ is 0.9647 V at 25 °C. The temperature coefficient is $1.74 \times 10^{-4} \text{ V K}^{-1}$. Calculate the value of ΔG , ΔS and ΔH .

$$[\text{Ans } \Delta G = -186.187 \text{ kJ}; \Delta S = 33.58 \text{ J K}^{-1}; \Delta H = -176.18 \text{ kJ}]$$

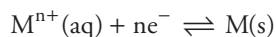
16.13 Types of Electrodes

A wide variety of electrodes are known. They are classified depending upon the nature of the half cell reactions. Some common types of reversible electrodes are discussed below.

1. **Metal-metal ion electrode** This type of electrode consists of a metal in contact with a solution of its own ions. These electrodes are also known as electrodes reversible with respect

to cations. Common examples are (i) Cu electrode in a solution of CuSO_4 (ii) Zn rod in a solution of ZnSO_4 .

A general electrode reaction of a metal in contact with the solution of its salt may be represented as



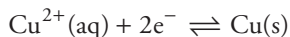
If the metal rod behaves as a positive electrode (i.e., reaction at electrode is a reduction reaction) the equilibrium shifts to the right and the concentration of M^{n+} ions in the solution will decrease. On the other hand, if the metal rod behaves as a negative electrode (i.e., the electrode reaction involves oxidation), the above equilibrium will shift to the left and the concentration of M^{n+} ions in the solution will increase. The electrode is thus reversible with respect to the M^{n+} ions.

From the Nernst equation we have

$$E_{\text{M}} = E_{\text{M}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{M}(\text{s})]}{[\text{M}^{n+}(\text{aq})]}$$

$$\text{or } E_{\text{M}} = E_{\text{M}}^{\circ} + \frac{2.303RT}{nF} \log [\text{M}^{n+}(\text{aq})] \quad \because [\text{M}(\text{s})] = 1$$

If the electrode is a Cu electrode in contact with CuSO_4 solution, the electrode reaction is



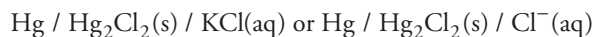
Then from the Nernst equation we have

$$E_{\text{Cu}} = E_{\text{Cu}}^{\circ} + \frac{2.303RT}{2F} \log [\text{Cu}^{2+}(\text{aq})] \quad \because \{[\text{Cu}(\text{s})] = 1 \text{ and } n = 2\}$$

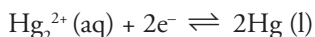
The electrode potential depends on the standard reduction potential of copper E_{Cu}° and the concentration of Cu^{2+} ions.

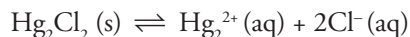
2. **Metal-insoluble salt electrode** In this type of electrode, the metal is in contact with its sparingly soluble salts and a solution of a soluble salt having an anion common with the sparingly soluble salt. These electrodes are reversible with respect to the anion. Common examples are (i) calomel electrode (ii) silver-silver chloride electrode (iii) lead-lead sulphate electrode

- (i) **Calomel electrode** It is commonly used as a secondary reference electrode for potential measurements in place of a hydrogen electrode. The calomel electrode consists of mercury in contact with mercurous chloride Hg_2Cl_2 (calomel) and a solution of soluble chloride ions such as KCl of known concentration. It is represented as

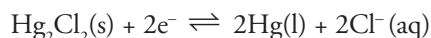


The half cell reaction is





Thus, in case of calomel electrode, the electrode reaction may be represented as



The electrode, therefore is reversible with respect to chloride ion.

The electrode potential is given by

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Hg}]^2 [\text{Cl}^-]^2}{\text{Hg}_2\text{Cl}_2}$$

∵ Hg is a pure liquid and Hg_2Cl_2 is a pure solid hence $[\text{Hg}] = 1$ and $[\text{Hg}_2\text{Cl}_2] = 1$

$$E = E^0 - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2$$

$$E = E^0 - \frac{2.303RT}{F} \log [\text{Cl}^-]$$

The electrode is constructed by placing a small amount of mercury in a glass vessel (Fig. 16.11). It is covered with a paste of solid Hg_2Cl_2 and mercury. This layer is further covered with a KCl solution of known concentration. A platinum wire dips into the mercury layer to make electrical contact. The side tube is used for making contact with the salt bridge. The potential of calomel electrode depends upon the concentration of KCl solution used.

Concentration of KCl solution	Electrode potential (reduction)
0.1 M KCl	0.334 volts (at 25 °C)
1.0 M KCl	0.280 volts (at 25 °C)
Saturated KCl	0.2422 volts (at 25 °C)

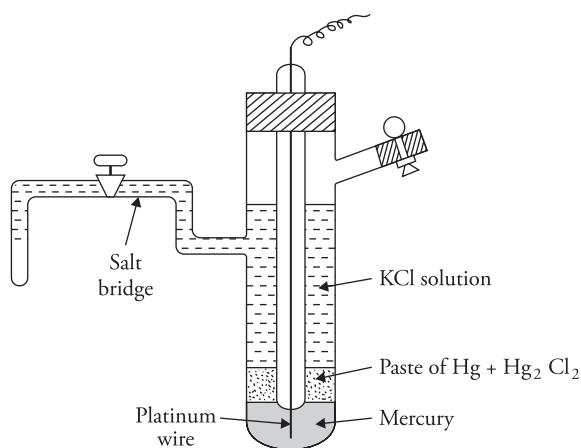
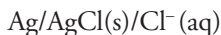


Figure 16.11 Calomel electrode

(ii) **Silver – silver chloride electrode**

It consists of a silver wire, coated electrolytically with silver chloride (a highly insoluble salt) and is dipped in a KCl solution (Fig. 16.12). The electrode is represented as



The electrode reaction is

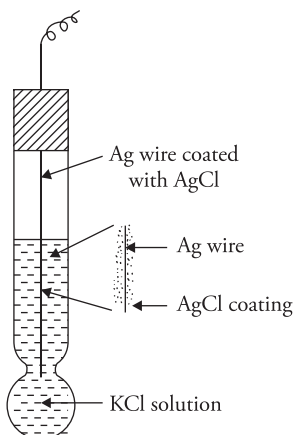
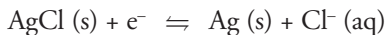


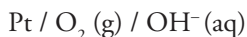
Figure 16.12 Ag–AgCl electrode

(iii) **Gas electrode**

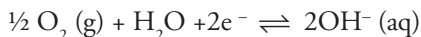
In these electrodes, gases (O_2 or Cl_2) are continuously bubbled through a solution of their corresponding ions, i.e., hydroxyl or chloride ions using an inert metal like Pt or Au to maintain electrical contact.

The inert metal is dipped in the solution of hydroxyl or chloride ions and the gas is bubbled. The metal adsorbs the gas and an equilibrium is established between the gas and the ions in the solution. Common examples of this type are the hydrogen electrode (refer to Section 16.9), oxygen electrode and chlorine electrode.

In oxygen electrode Oxygen gas is bubbled through a solution containing OH^- ions and a platinum strip is dipped in it. The cell is represented as



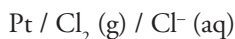
The electrode reaction is



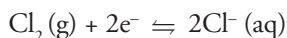
The electrode is reversible with respect to OH^- ions. However, due to the formation of an oxide film on the metal, equilibrium cannot be established easily, hence oxygen electrode does not behave as a truly reversible electrode.

In chlorine electrode Chlorine gas is bubbled through a solution containing Cl^- ions in HCl solution. An inert Pt strip is dipped in the solution to maintain electrical contact.

The cell is represented as –



The electrode reaction is



This electrode is reversible with respect to Cl^- ions

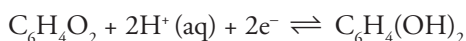
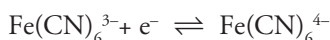
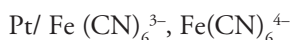
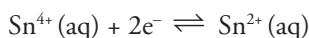
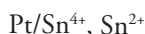
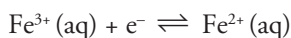
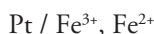
Hydrogen electrode Refer to Section 16.9.

(iv) **Oxidation Reduction Electrodes**

Although oxidation and reduction reactions occur in the two half cells of all galvanic cells yet the term oxidation reduction electrode is used for those electrodes in which the potential is developed due to the presence of ions of the same substance in two different valence states in contact with an inert metal electrode like platinum or gold. The unattackable metal acts as the conductor of electrons and is used for making electric contact, its purpose is only to supply or accept electrons. Common examples are platinum wire dipped in a solution containing Fe^{2+} and Fe^{3+} ions or $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ ions or Sn^{2+} and Sn^{4+} ions or quinhydrone, i.e., hydroquinone and quinone together with hydrogen ions. The electrode and the half cell reaction are as follows

Electrode

Half cell reaction



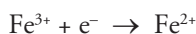
Q = Quinhydrone

The electrode potential is given by

$$E_{\text{redox}} = E_{\text{redox}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Reduced state}]}{[\text{Oxidized state}]}$$

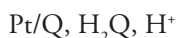
For example, the redox potential of the cell

$\text{Pt} / \text{Fe}^{3+}, \text{Fe}^{2+}$ can be expressed as–

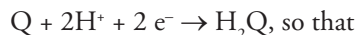


$$E_{\text{redox}} = E_{\text{redox}}^0 - \frac{2.303RT}{F} \log_{10} \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad \because n = 1$$

Quinhydrone electrode Quinhydrone is a 1:1 molecular complex of quinone (represented as Q) and hydroquinone represented as H_2Q . The electrode may be represented as



It is reversible with respect to H^+ ions. It involves a reversible reaction between quinone (Q) and hydroquinone (H_2Q). The reduction reaction at this electrode is expressed as



$$E_{Pt/Q, H_2Q, H^+} = E^\circ - \frac{2.303RT}{2F} \log_{10} \frac{[H_2Q]}{[Q][H^+]^2}$$

\because [Q] and $[H_2Q]$ are in equimolar concentration, the above expression can also be written as

$$E_{Pt/Q, H_2Q, H^+} = E^\circ + \frac{2.303RT}{F} \log_{10} [H^+]$$

Quinhydrone electrode behaves as a form of hydrogen electrode and is used for measuring the pH of solutions as an indicator electrode.

To make a quinhydrone electrode, quinhydrone is dissolved in a solution whose pH is to be determined until the solution becomes saturated and a platinum wire is immersed in it.

(v) Membrane electrodes

These electrodes are sensitive to a particular ion species and hence a potential develops. In these electrodes, a semi-permeable membrane separates two solutions of a salt at different concentrations. The semi-permeable membrane permits the passage of only one type of specific ion, thereby developing a potential with respect to that species. The other species are totally ignored.

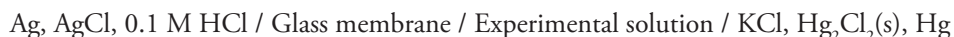
Since the membranes are selective to specific ions, these electrodes are also termed as ion selective electrodes. A typical example of this type is the glass electrode which is selective to H^+ ions.

Glass electrode It is the most useful and versatile of all electrodes used for pH measurements. It is based on the principle that when two solutions of different hydrogen ion concentrations are separated by a glass membrane, a potential difference develops across the glass membrane. The magnitude of the potential difference depends upon the difference in the concentration of the hydrogen ions in the two solutions. The glass membrane is a special type of membrane having the approximate composition of 72% SiO_2 , 22% Na_2O and 6% CaO .

A glass electrode consists of a thin walled bulb of pH sensitive glass sealed to a stem of non-pH sensitive high resistance glass (Fig. 16.13). Inside the glass electrode is a silver-silver chloride electrode or calomel electrode in 0.1 M HCl solution.

This glass electrode is dipped in a solution of varying hydrogen ion concentration (unknown pH) and is connected to an external reference electrode, usually a calomel electrode, with the help of a salt bridge.

The cell may be represented as



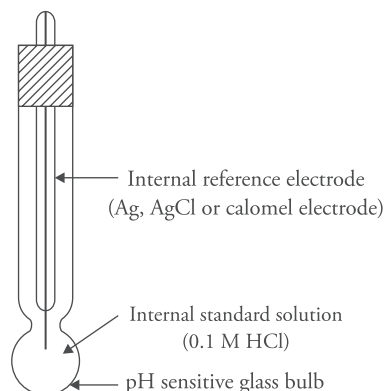


Figure 16.13 *Glass electrode*

Nowadays, combined electrodes are generally used. A combined electrode is one in which the pH sensitive glass electrode and the reference electrode are built together. In such an arrangement, the internal reference electrode inside the glass electrode and the external reference electrode outside the glass electrode connected by a salt bridge are identical (Fig. 16.14). Both reference electrodes may be silver / silver chloride type or calomel electrodes.

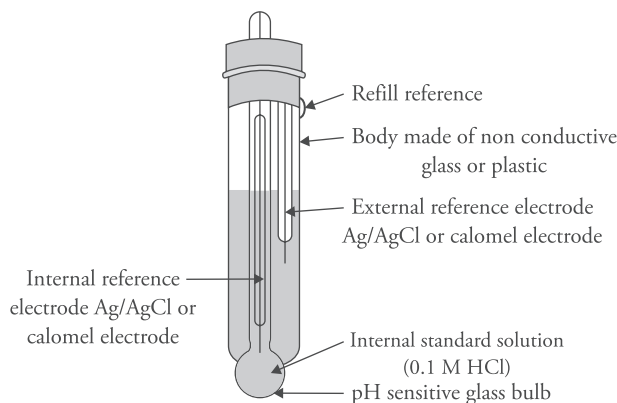


Figure 16.14 *Combination electrode*

16.14 Determination of Fluoride by Ion Selective Electrode Method

An ion selective membrane is called so as it permits preferentially the movement of some specific type of ions over the other ions. Electrodes using such membranes are termed as ion selective electrodes. An ion selective electrode consists of an internal reference electrode and a membrane that acts as an interface between the sample solution and the ISE. A potential develops across the membrane that depends on the difference in the concentration/activity of the specific ion. The concentration of the internal reference solution being fixed; the developed potential is directly proportional to the concentration of the sample solution. The most common example of ion

selective electrode is the glass electrode having a glass membrane that permits the movement of H^+ ions preferentially.

An ISE for the determination of fluoride ion uses a Ag/AgCl reference electrode immersed in KCl solution (3 M) and saturated AgCl solution in conjunction with a fluoride ISE. A combination electrode consisting of these two electrodes in a common casing is commonly used these days. The fluoride selective membrane is made of a single crystal of LaF_3 doped with Europium (II) ion to increase the conductivity of the membrane. This membrane selectively permits the movement of F^- ions over the other ions. A potential thus develops across the membrane and this potential is proportional to the concentration of fluoride ions. It is measured with the help of a pH meter or an ionmeter.

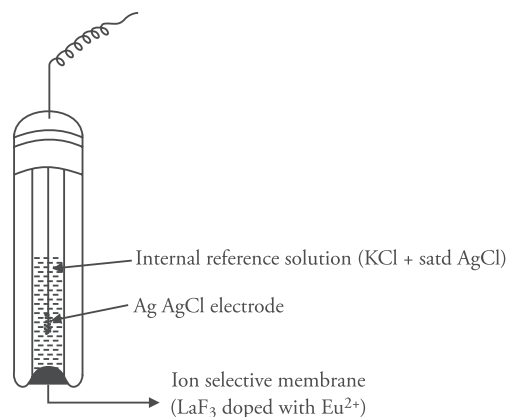


Figure 16.15 Fluoride ion selective electrode

Interferences

- The size of OH^- ion is similar to that of the F^- ion and hence it can also migrate across the LaF_3 membrane producing a potential. It has been found that the electrode becomes cross sensitive to OH^- ions at a pH above 8 hence pH control is essential for fluoride ISE measurements.
- At low pH fluoride ion combines with hydrogen ions producing HF and HF_2^- which cannot diffuse through the LaF_3 membrane owing to their large size. This decreases the results for fluoride ions at pH 5 or less. The ideal pH for fluoride ion determination is 5.5
- Polyvalent ions like Ca^{2+} , Cu^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , Si^{4+} bind the fluoride ions making them inaccessible for measurement by fluoride ISE. The effect of polyvalent ions is minimised by the addition of TISAB (Total ionic strength adjustment buffer) [TISAB is a mixture of acetate buffer at pH 5 to 5.5, 1 M NaCl and cyclohexylenedinitrilotetraacetic acid CDTA. CDTA is a complexing agent like EDTA and helps to minimise interference of polyvalent ions like Ca^{2+} , Cu^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , Si^{4+} by forming complexes]

Determination of F^- ions

A stock solution of fluoride ions (1000 ppm) is prepared by dissolving required amount of NaF (dried for 1 hour in the oven). Standard solutions of 100 ppm, 50 ppm, 10 ppm, 2 ppm and 1

ppm are prepared from this stock solution by serial dilution into a 100 mL flask. To measure the fluoride ion concentration the standard solution and TISAB in ratio 1:1 are taken in the beaker and the combined electrode is dipped in it and the reading is noted using a pH meter in mV mode. A calibration curve is obtained by plotting the log of fluoride ion concentration and the potential in mV. Now the sample solution with TISAB in the ratio 1:1 is taken and the potential in mV is noted using the pH meter. The concentration of the sample solution can be obtained by plotting this value on the calibration curve.

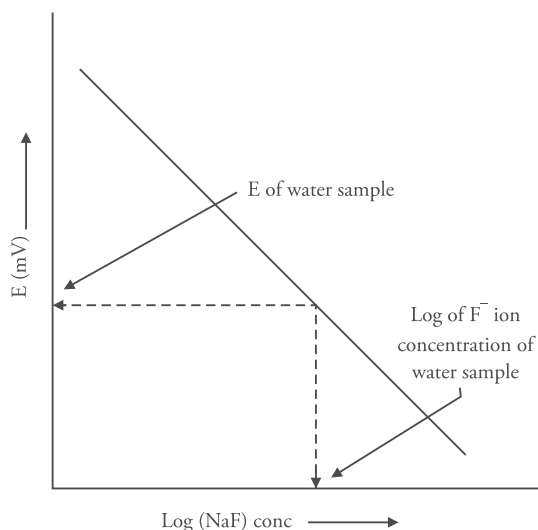


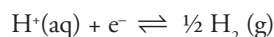
Figure 16.16 Calibration curve for fluoride determination

16.15 Determination of pH

The pH can be determined with the help of indicator electrodes reversible with respect to H^+ ions like (i) hydrogen electrode (ii) quinhydrone electrode (iii) glass electrode

(i) Use of hydrogen electrode

For pH determination, the cell is made up of two hydrogen half cells. A platinum electrode is dipped into the solution whose pH is to be determined instead of 1 N HCl, and H_2 gas at 1 atm is passed over the platinum electrode. The electrode reaction is



$$\text{The electrode potential is given by } E_{H^+/H_2} = E_{H^+/H_2}^0 - \frac{2.303RT}{nF} \log_{10} \frac{[H_2]^{1/2}}{[H^+]}$$

$$\because [H_2] = 1, \quad E^0 = 0, \quad n = 1 \quad \text{therefore}$$

$$E_{H^+/H_2} = -0.0591 \log \frac{1}{[H^+]}$$

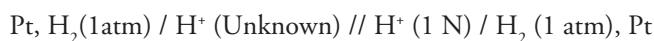
$$\text{or } E_{\text{H}^+/\text{H}_2} = 0.0591 \log[\text{H}^+]$$

$$E_{\text{H}^+/\text{H}_2} = -0.0591 \text{pH at } 25^\circ\text{C} \quad (1)$$

$$\therefore \text{pH} = -\log[\text{H}^+]$$

This half cell is connected by a salt bridge to a standard hydrogen electrode having a solution of 1 N HCl.

The cell may be represented as



EMF of the above cell,

$$E_{\text{observed}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= E_{\text{right}} - E_{\text{left}}$$

$$\therefore E_{\text{right}} = 0$$

$$E_{\text{observed}} = -E_{\text{left}}$$

$$E_{\text{observed}} = -(-0.0591 \text{pH})$$

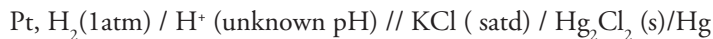
or

$$\text{pH} = \frac{E_{\text{observed}}}{0.0591}$$

Thus, pH can be calculated using the above equation.

However, since it is difficult to set a hydrogen electrode, pH is generally measured using either a quinhydrone electrode or a glass electrode

If a hydrogen electrode is coupled with a saturated calomel electrode, then the cell is formulated as



$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{H}^+/\text{H}_2} \quad (2)$$

$$\text{from eq.(1) } E_{\text{H}^+/\text{H}_2} = -0.0591 \text{pH}$$

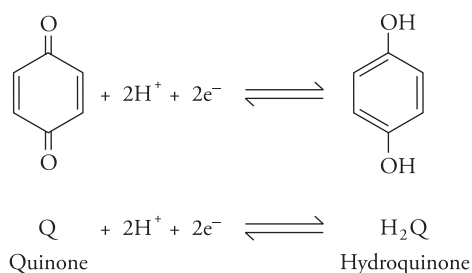
For a saturated calomel electrode, the reduction electrode potential is 0.2422 volts. Placing these values in Eq. (2), we have

$$E_{\text{cell}} = 0.2422 - (-0.0591 \text{ pH})$$

$$\text{or } \text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591}$$

(ii) **Quinhydrone electrode**

As discussed earlier (Section 16.13) the reduction reaction for quinhydrone is expressed as



The electrode potential is given by

$$E_{\text{Q}} = E_{\text{Q}}^0 - \frac{0.0591}{n} \log \frac{[\text{H}_2\text{Q}]}{[\text{Q}][\text{H}^+]^2}$$

$$\because [\text{H}_2\text{Q}] = 1 \quad \text{and} \quad [\text{Q}] = 1. \quad n = 2$$

$$E_{\text{Q}} = E_{\text{Q}}^0 - \frac{0.0591}{2} \log \frac{1}{[\text{H}^+]^2}$$

$$E_{\text{Q}} = E_{\text{Q}}^0 + \frac{0.0591}{2} \times 2 \log [\text{H}^+]$$

$$E_{\text{Q}} = E_{\text{Q}}^0 + 0.0591 \log [\text{H}^+]$$

$$E_{\text{Q}} = E_{\text{Q}}^0 - 0.0591 \text{ pH}$$

At 25 °C, the reduction potential E^0 is 0.6994, hence

$$E_{\text{Q}} = 0.6994 - 0.0591 \text{ pH}$$

This cell is combined with a calomel electrode and the EMF of the combination is determined using a potentiometer (Fig. 16.17).

$\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}), \text{KCl} (\text{satd solution}) // \text{H}^+ (\text{unknown}) \text{Q}, \text{QH}_2 / \text{Pt}$

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$= E_{\text{quinhydrone}} - E_{\text{calomel}}$$

$$E_{\text{cell}} = 0.6994 - 0.0591 \text{ pH} - 0.2422 \quad (\text{reduction potential of saturated calomel electrode} = 0.2422)$$

$$\text{pH} = \frac{0.6994 - 0.2422 - E_{\text{cell}}}{0.0591}$$

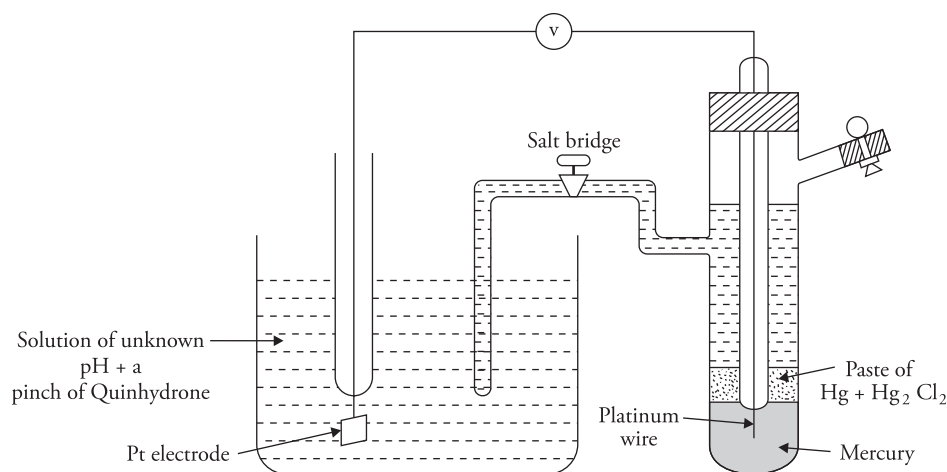


Figure 16.17 Determination of pH by Quinhydrone electrode

(iii) Glass electrode

The half cell for a glass electrode is

$\text{Ag} / \text{AgCl}(\text{s}), \text{HCl} (0.1 \text{ M}) / \text{glass}$

$$E_{\text{glass}} = E_{\text{glass}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{H}_2]^{1/2}}{[\text{H}^+]}$$

$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.0591 \log \frac{1}{[\text{H}^+]}$$

$$E_{\text{glass}} = E_{\text{glass}}^0 - 0.0591 \text{ pH}$$

To find pH, this is coupled with a calomel electrode (Fig 16.18). The cell is formulated as
 $\text{Ag} / \text{AgCl (s)} / \text{HCl (0.1 M)} / \text{glass} // \text{solution of unknown pH} / \text{calomel electrode}$
 (The electrode potentials are expressed as reduction potentials)

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$E_{\text{cell}} = E_{\text{calomel}} - (E_{\text{glass}}^0 - 0.0591 \text{ pH})$$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}^0 + 0.0591 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - E_{\text{calomel}} + E_{\text{glass}}^0}{0.0591} \text{ at } 25^\circ\text{C}$$

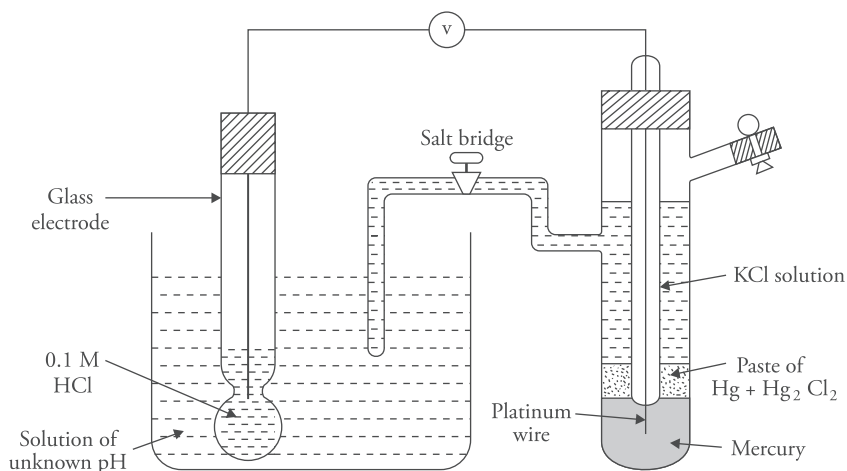


Figure 16.18 Determination of pH by glass electrode

Solved examples

- At 25°C , the EMF of the cell
 $\text{Pt, H}_2(1 \text{ atm}) / \text{H}^+(\text{Unknown}) // \text{KCl (satd)} / \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}$ is 0.445 volts. Calculate the pH of the solution.

Solution

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{H}_2}$$

$$0.445 = 0.2422 - E_{\text{H}_2} \quad (\text{for a satd calomel electrode } E_{\text{calomel}} = 0.2422)$$

$$\text{or } E_{\text{H}_2} = -0.2028 \quad (\text{i})$$

For a hydrogen electrode

$$E_{\text{H}^+/\text{H}_2} = -0.0591 \log \frac{1}{[\text{H}^+]} \quad (\text{ii})$$

Equating (i) and (ii)

$$-0.0591 \log \frac{1}{[\text{H}^+]} = -0.2028$$

$$\text{or } -0.0591 \text{ pH} = -0.2028$$

$$\text{pH} = \frac{0.2028}{0.0591} = 3.431$$

Alternate method by direct formula application

$$\text{pH} = \frac{E_{\text{cell}} - 0.2422}{0.0591} = \frac{0.445 - 0.2422}{0.0591} = 3.431$$

2. The EMF of the cell $\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}), \text{KCl} (\text{satd}) // \text{H}^+ (\text{unknown})$ with quinhydrone / Pt is 0.264 volts at 25 °C. Find the pH of the solution if

$$E_{\text{calomel}} = 0.2422 \text{ V}; \quad E_{\text{Q}}^0 = 0.6996 \text{ V}$$

Solution

$$E_{\text{cell}} = E_{\text{Q}} - E_{\text{calomel}}$$

$$\text{and } E_{\text{Q}} = E_{\text{Q}}^0 - 0.0591 \text{ pH}$$

$$E_{\text{cell}} = E_{\text{Q}}^0 - 0.0591 \text{ pH} - E_{\text{calomel}}$$

$$0.264 = 0.6996 - 0.0591 \text{ pH} - 0.2422$$

$$0.0591 \text{ pH} = 0.6996 - 0.2422 - 0.264$$

$$\text{pH} = \frac{0.6996 - 0.2422 - 0.264}{0.0591} = 3.2724$$

Practice problems

- Find the pH of a solution placed in a quinhydrone half cell which was coupled with standard calomel electrode. The EMF of the combined cell was determined to be 0.123 V at 25 °C.

$$E_{\text{calomel}} = 0.2415 \text{ V}; \quad E_{\text{Q}}^0 = 0.6996 \text{ V} \quad [\text{Ans } 5.67]$$

- The EMF of the cell

Pt / H₂(g) (1 atm) / Buffer // normal calomel electrode is 0.5164 volts at 25 °C . Given that the reduction potential of a normal calomel electrode is 0.2800 volts, calculate pH of the buffer. [Ans 4]

16.16 Concentration Cells

The electric energy produced in a galvanic cell is due to the chemical reaction occurring in the cell. There is another type of cell called a 'concentration cell' in which there is no chemical reaction. Electrical energy is produced due to the transfer of matter from a region of higher concentration to a region of lower concentration (around the electrodes). Chemical reactions, of course, occur at different electrodes but they are such that the chemical change occurring in one half cell is exactly balanced by the reverse chemical change occurring in the other half cell, resulting in no net chemical change in the cell. The net process is therefore, a purely physical change involving the levelling of concentration difference between the different regions of the cell.

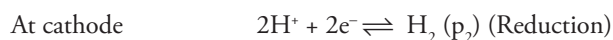
The concentration cells are of two types.

- Electrode concentration cells.
 - Electrolyte concentration cells.
- Electrode concentration cells** In these cells, two identical electrodes of different concentrations are dipped in the same solution of electrolyte containing ions of the electrode material. Amalgam electrode and gaseous electrodes are examples of this type. Two hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute an electrode concentration cell. The electrode with the higher pressure of gas forms the anode. The cell may be represented as



where $p_1 > p_2$

The cell reactions are



The net reaction is independent of the concentration of the electrolyte. The cell reaction merely involves the transfer of hydrogen gas from higher pressure (p_1) to lower pressure (p_2)
The EMF of the cell is

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

Since E° in concentration cells is zero and n for the above cell reaction is 2, therefore—

$$E = -\frac{0.0591}{2} \log \frac{p_2}{p_1} = 0.02955 \log \frac{p_1}{p_2} \text{ at } 25^\circ \text{C}$$

- (ii) Consider two amalgams of silver at different concentrations c_1 and c_2 in contact with silver nitrate solution. The cell may be represented as



where $c_1 > c_2$. The cell reactions are



The EMF of the cell is

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{c_2}{c_1}$$

$E^\circ = 0$. Hence,

$$E = -0.0591 \log \frac{c_2}{c_1} \quad \because n = 1$$

$$E = 0.0591 \log \frac{c_1}{c_2}$$

when $c_1 = 1$ and $c_2 = 1$, the two electrode systems will be same and no current will flow.

2. **Electrolyte concentration cells** A cell of this type consists of two identical electrodes in contact with a solution of the same electrolyte but at different concentrations. Since the concentration of electrolyte is different at the two electrodes, their electrode potential will be different.

Depending on the way in which the two solutions of different concentrations are put in physical contact, two situations arise.

- (i) **When the two solutions are in direct contact with each other** The ions of the electrolyte tend to diffuse from the concentrated solution to the dilute solution. A potential called liquid-liquid junction potential develops at the junction of the two

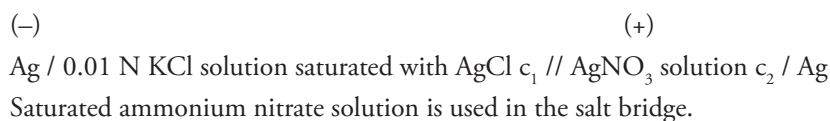
solutions. This is taken into account while computing the EMF of the cell. The cells of this type are called *concentration cells with transference* or *concentration cells with liquid junction potential*.

- (ii) **When the solutions are not in direct contact with each other** Such cells have no liquid junctions and hence no direct transfer of the electrolyte occurs from one solution to the other. They are called *concentration cells without transference* or *concentration cells without liquid junction potential*.

Applications of concentration cells

1. Determination of the solubility product of a sparingly soluble salt like AgCl.

The following cell is set up:



Electrode reactions are:



$$\begin{aligned} E_{\text{cell}} &= -\frac{RT}{nF} \ln \frac{c_1}{c_2} \\ &= \frac{2.303RT}{nF} \log \frac{c_2}{c_1} \end{aligned}$$

E_{cell} is determined. The concentration of AgNO_3 , i.e., c_2 is known. By substituting the value in the equation, c_1 can be evaluated. c_1 is the concentration of Ag^+ ions furnished by AgCl in KCl solution. If 0.01 N KCl is assumed to be completely ionised, then $[\text{Cl}^-] = 0.01$

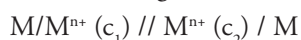
$\therefore K_{\text{sp}}$, the solubility product of AgCl = $[\text{Ag}^+] [\text{Cl}^-]$

$$= c_1 \times 0.01$$

Then, solubility of AgCl = $s = \sqrt{c_1 \times 0.01} \text{ mol L}^{-1}$

2. Determination of valency of an ion

Consider the general cell,



The cell reaction is



$$E_{\text{cell}} = -\frac{2.303RT}{nF} \log \frac{c_1}{c_2}$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

Placing the values of E_{cell} , c_1 and c_2 , the valency can be calculated.

Solved examples

Calculate the potential of the following concentration cell at 25 °C.

Pb (Hg) ($c_1 = 0.5$) / $\text{Pb}(\text{NO}_3)_2$ solution / Pb(Hg) ($c_2 = 0.05$)

Solution

The EMF is given by the expression

$$E_{\text{cell}} = -\frac{RT}{nF} \log \frac{c_2}{c_1} = \frac{0.0591}{2} \log \frac{c_1}{c_2}$$

(Here $n = 2$, $c_1 = 0.5$, $c_2 = 0.05$, hence

$$E_{\text{cell}} = 0.0295 \log \frac{0.5}{0.05} = 0.0295 \log 10 = 0.0295 \text{ V}$$

16.17 Batteries

By now, we would be well aware of the chemical reactions that lead to the production of electricity in an galvanic cell. This energy is stored in the cell and can be used when required. A battery is a power source in which several galvanic cells are connected in series. When two or more cells are connected in series or parallel, it constitutes a battery. Like a galvanic cell, a battery also consists of an anode, a cathode and an electrolyte. There are three types of batteries.

- (i) Primary batteries
- (ii) Secondary batteries
- (iii) Reserve batteries

Primary batteries (or primary cells) In these batteries, the cell reaction is irreversible, i.e., the reaction taking place in the forward direction cannot be reversed by the application of external potential. Once the cell reaction has taken place and the reactants have been converted into products, the cell gets discharged and cannot be used again. Example: Dry cells or Leclanche cell.

Secondary batteries (or secondary cell) In these batteries, the cell reaction is reversible. Once the forward reaction occurs and the cell is discharged, it can be charged again by applying external

potential. They are also called storage cells or rechargeable batteries. Common examples are lead acid batteries used in automobiles, nickel cadmium batteries used in aircraft and railways and lithium ion batteries used in mobile phones.

Reserve batteries These are batteries which remain in an inactive state and are activated immediately before use. Activation is done by adding the missing component like by the simple addition of water or any other electrolyte. These batteries are very useful in mines, radars, night viewing equipments, artillery, pilot balloons, etc. They should withstand vibration, shock, extreme pressure variation; have a long inactive shelf life and should be rapidly activated when required. Common examples are silver chloride cells which are activated by sea water or even by fresh water. They can also be activated by

- Mechanical means
- Thermal activation
- Use of an electrolyte or solvent

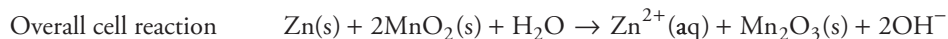
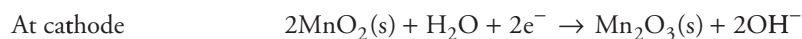
Classical batteries

1. Dry battery (Leclanche cell)

It is called a dry battery as it does not have any liquid electrolyte in it. The zinc vessel serves as the anode (Fig. 16.19). The cathode is a graphite rod in the centre of the cell. It is surrounded by the electrolyte which consists of a paste of NH_4Cl , ZnCl_2 , MnO_2 . Traces of acetylene black, graphite powder are also added. Starch is added to make the mixture like a thick paste. The cell is represented as

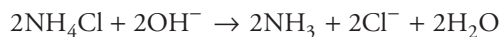


The reactions taking place at the anode and cathode are as follows:



Some secondary reactions also occur. The hydroxyl ions formed at the cathode react with NH_4Cl to liberate NH_3 which reacts with Zn^{2+} ions to form a complex $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2(\text{s})$.

The secondary reactions are as follows:



Crystals of $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2(\text{s})$ formed by the interaction of free NH_3 precipitate out shielding the active material of both the electrodes. This leads to the deterioration of the cell parameters and the cell voltage drops.

Applications The cell is a primary cell, and gives a voltage of 1.5 V. These cells are used in transistors, tape recorders, toys, portable electronic gadgets.

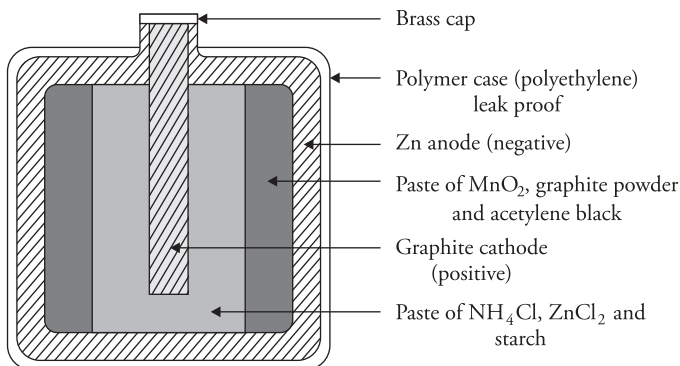
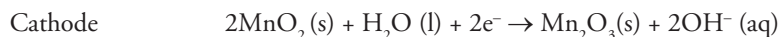


Figure 16.19 Dry cell

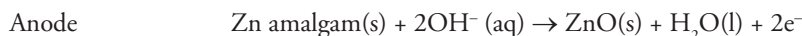
2. **Alkaline battery** These batteries use an alkaline electrolyte. In a zinc– MnO_2 battery which is a modification of the dry cell, NH_4Cl has been replaced by KOH or NaOH and serves as an electrolyte. Replacing NH_4Cl by KOH or NaOH prevents corrosion of zinc electrode since zinc does not dissolve in basic medium. The body of the battery is made up of zinc cylinder and serves as anode. The graphite cathode is surrounded by a paste of MnO_2 . KOH is mixed with zinc powder and surrounds the MnO_2 layers. The cell can be represented as



The life of this battery is longer than the dry cell because zinc does not corrode. It gives a voltage of 1.5 V.

Applications It is mainly used in cameras, calculators, watches, etc.

3. **Mercury battery** These are tiny cells used for specialized medical applications in advanced electronics. Anode is made of zinc amalgam (a solution of Zn in mercury), cathode is made of a paste of mercuric oxide with some amount of graphite. Paste of zinc oxide and potassium hydroxide forms the electrolyte. The anode and cathode are separated by a cellulose (paper) which acts as absorbing material for the electrolyte. Paper permits migration of ions. The entire cell is covered in a stainless steel case. The cell reactions are

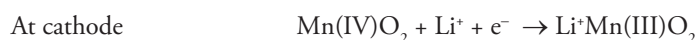


Application These cells are small and expensive. They are used in pacemakers, hearing aids, digital watches, etc.

4. **Lithium–MnO₂ batteries** These are primary batteries that cannot be recharged. In these batteries lithium metal or lithium compounds are used as anode. The cathode is made of specially treated MnO₂ crystals obtained by special heat treatment (Fig. 16.20). Since lithium is highly reactive with water and non-aqueous solvents, these solvents cannot be used as electrolyte. Instead, lithium salt solution in propylene carbonate and dimethoxy salts is used as the electrolyte. Solvents like thionyl chloride containing lithium compounds such as LiCl, LiBr, LiAlCl₄, LiSO₃CF₃, LiClO₄ can also be used. The cell can be represented as

Li / Non-aqueous solvent containing lithium salts / MnO₂

The cell reactions are



Lithium batteries find use in clocks, calculators, toys, digital cameras, watches, medical equipments like artificial pacemakers, thermometers, and remote car locks, etc.

(–) Li anode	Li ⁺ Polymer Electrolyte	(+) MnO ₂ cathode
--------------------	--	---------------------------------

Figure 16.20 *Li–MnO₂ battery*

Secondary cells

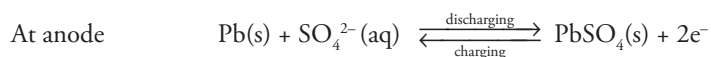
The chemical reactions in secondary cells are reversible. They can be recharged. Secondary cells are also known as storage cells or rechargeable batteries. Common examples are Ni–Cd batteries and lead acid batteries commonly used in cars.

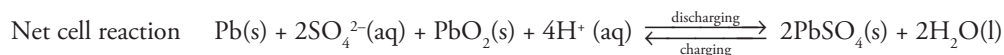
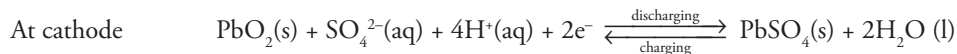
- (i) **Lead acid battery / lead accumulator** A lead acid battery consists of a rectangular ebonite or polymeric case which contains 5 M sulphuric acid (37 per cent). Both the electrodes are made of lead grids separated by microporous polyethylene (Fig. 16.21). The anode is coated with spongy lead and the cathode is coated with a paste of spongy lead and lead dioxide in the ratio 1:1. Six such pairs of anode and cathode are placed in series. The terminals are welded and the case is sealed.

The cell is represented as



The cell reactions are





In this battery, the voltage of each cell is 2 V. Hence the total voltage of six cells in series is nearly 12 volts. As evident from the cell reaction, water is formed as a product; hence sulphuric acid gets diluted during discharging. The extent to which the battery is discharged can be checked by measuring the density of H_2SO_4 by hydrometer. It can be charged again.

As the battery is used, lead is gradually converted to insoluble lead sulphate at the electrodes. When both the electrodes are converted to lead sulphate, the battery gets totally discharged and cannot be recharged. Actually, a lead storage cell functions both as a voltaic cell and an electrolytic cell. When electricity is drawn from the cell, it behaves as a voltaic cell; when the car is running, the cell is recharged and it acts as an electrolytic cell.

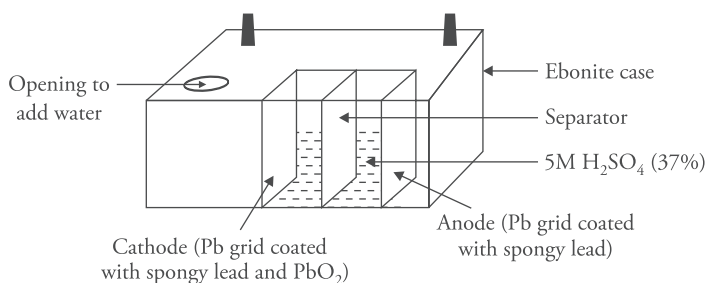
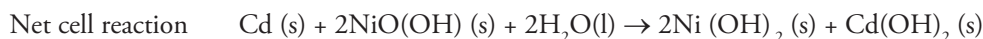


Figure 16.21 Pb-acid battery

- (ii) **Nickel cadmium battery** It is a secondary alkaline storage battery that consists of anode grid consisting of spongy cadmium with cadmium hydroxide (Fig. 16.22). The cathode is composed of a paste of nickel oxyhydroxide $\text{NiO}(\text{OH})$ (s) and small amount of graphite to increase electrical conductivity. The electrolyte used is 5 M KOH solution. The cell may be represented as

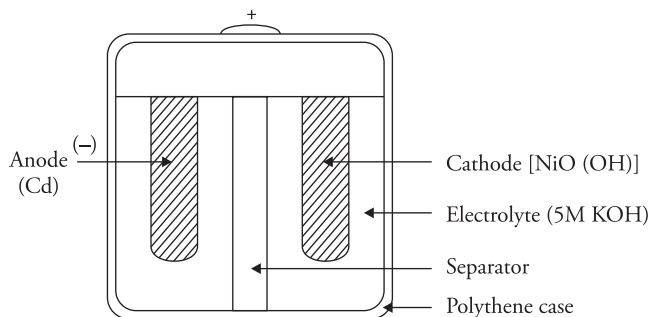


The cell reactions are



Its voltage is ~ 1.35 V. However, its voltage is fairly constant. The reaction products adhere to the electrode surface and the reaction can be easily reversed. This type of battery does not undergo deterioration as no gases are produced. It is light, portable and rechargeable.

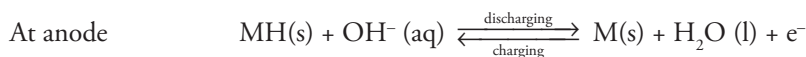
Applications It is used in calculators, electronic flash units, cordless shavers, transistors, etc.

**Figure 16.22** *Nicad cell*

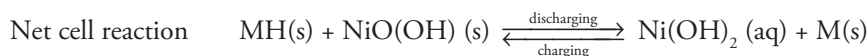
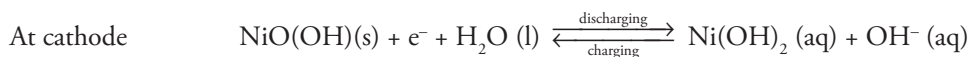
- (iii) **Nickel metal hydride batteries (NiMH)** Like nickel cadmium cells, these are rechargeable batteries. However, instead of cadmium anode, these batteries contain hydrogen absorbing alloys like zirconium hydride ZrH_2 , vanadium hydride VH_2 , titanium hydride TiH_2 , absorbed on an alloy of LaNi_5 and TiAl (Fig. 16.23). These are then coated on the nickel foil or grid. The cathode is also a nickel foil coated with nickel hydroxide and nickel oxyhydroxide. Polypropylene is used as a separator and 5 M potassium hydroxide solution is used as an electrolyte. The electrodes together with the electrolyte are placed in a rectangular steel container which is completely sealed. The cell is represented as

$\text{MH} / \text{KOH} (5 \text{ M}) / \text{Ni}(\text{OH})_2, \text{NiO}(\text{OH})$

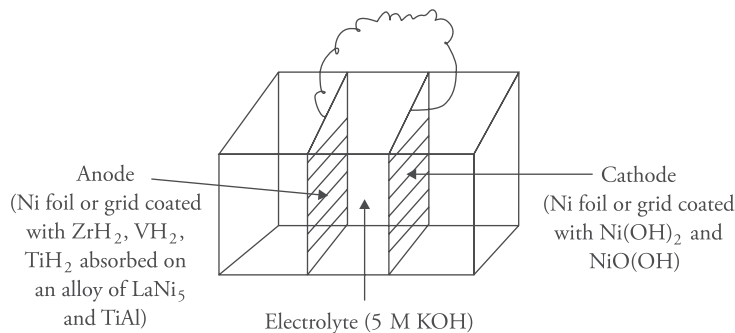
The cell reactions are



MH is a metal hydride and M, the metal

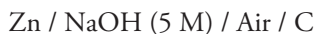


Applications These batteries are inexpensive and are used in cameras, medical instruments, electric toothbrushes, razors, mobile phones, pagers, etc

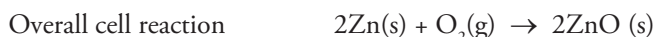
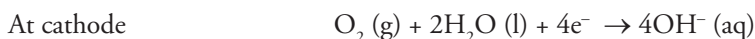
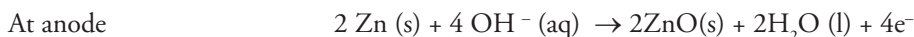
**Figure 16.23** *Nickel metal hydride battery*

- (iv) **Zinc air battery** In zinc air battery, the anode is made of zinc plates. A perforated carbon plate treated with water repellants acts as a cathode (Fig. 16.24). Sodium hydroxide (5 M) or potassium hydroxide is used as an electrolyte. The anode, cathode and the electrolyte are contained in an ebonite or polymeric case. It also has a vent for the entry of air or O_2 into the cell. At the anode, zinc reacts with electrolyte (NaOH or KOH) to form zincate ions which decay into zinc oxide and water. The electrons released at the anode travel to the cathode where oxygen of the air accepts the electrons to form hydroxide ions.

The cell is represented as



The cell reactions are



They produce 1.65 volts. Zinc air batteries have the properties of both fuel cell and batteries. Zinc air batteries are electrically non-rechargeable, however they can be recharged mechanically by converting the zinc oxide produced in the battery back into zinc metal. This zinc metal can be reused. They are very cheap and are increasingly being used instead of mercury batteries. Their size varies from small button cells that are used in watches and in hearing aids to large batteries used in cameras and also for the electric propulsion of vehicles.

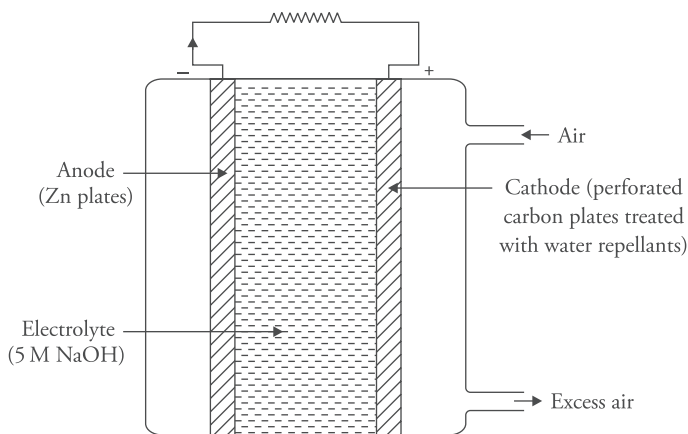


Figure 16.24 Zinc-air battery

Reserve battery

Magnesium–copper reserve battery These are made up of magnesium and cuprous chloride. Magnesium acts as anode and cuprous chloride serves as a cathode. The battery can be activated simply by the addition of sea water or tap water. It works on the principle of depositing copper metal onto the magnesium anode. The cell reactions are

At anode $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$

At cathode $2\text{Cu}^+ + 2\text{e}^- \rightarrow 2\text{Cu}$

Overall cell reaction $\text{Mg} + 2\text{CuCl} \rightarrow \text{MgCl}_2 + 2\text{Cu}$

Other salts that react with magnesium such as silver chloride, lead chloride, cuprous iodide or copper thiocyanate can be used instead of copper chloride.

The cell potential is in the range of 1.5–1.6 volts.

16.18 Fuel Cells

Fuel cells are energy converters which take chemical substances from the external source and convert them to electrical energy. Fuel cell differs from a battery in that the chemical substances are an integral part of a storage battery whereas in fuel cells, they are fed into the cells whenever energy is desired. The electrodes used in fuel cells are generally inert but have catalytic properties. The anodic materials used are generally gaseous or liquids (contrary to metal anodes used in batteries).

In a fuel cell, hydrogen enters at the anode where it loses electrons. These electrons travel to the cathode. Oxygen enters at the cathode. It picks up electrons and either

- Combines with the hydrogen ions that travel from the anode through the electrolyte or
- Travels to the anode through the electrolyte and combines with hydrogen ions.

The hydrogen and oxygen ions combine to form water which is removed from the cell. A fuel cell generates electricity as long as hydrogen and oxygen are supplied to it.

The electrolyte plays a vital role in a fuel cell. It permits appropriate ions to pass between the anode and cathode. Depending on the type of electrolyte used, there can be different types of fuel cells. They are listed below.

- Hydrogen–oxygen fuel cells
- Phosphoric acid fuel cells
- Molten carbonate fuel cells
- Solid polymer electrolyte fuel cells
- Solid oxide fuel cells

Liquid electrolyte is used in the first three fuel cells whereas the last two use solid electrolyte.

Some cells use pure hydrogen, hence a ‘reformer’ is employed to purify the fuel. Some fuel cells can accept impurities but their efficient working requires a high temperature. Let us discuss these five types of fuel cells one by one.

Hydrogen–oxygen fuel cell

Hydrogen–oxygen fuel cell consists of porous screens of graphite coated with a layer of platinum catalyst (Fig. 16.25). The technology employed is proton exchange membrane fuel cell (PEMFC)

technology. The electrolyte is a polymeric ion exchange membrane (polystyrenesulphonic acid or polymeric forms of perfluorosulphonic acid can be used). Moisture is to be supplied to keep the membrane wet hence the water balance is maintained in the resin by means of a wick. The water formed during the cell reaction is drained out and used for drinking. Several such cells are connected together to obtain the desired voltage.

Electrode reactions



The EMF of the cell at 25 °C is about 1.2 V. The above cell uses solid electrolyte and hence is called a solid polymer electrolyte cell. These cells are used in spacecrafts.

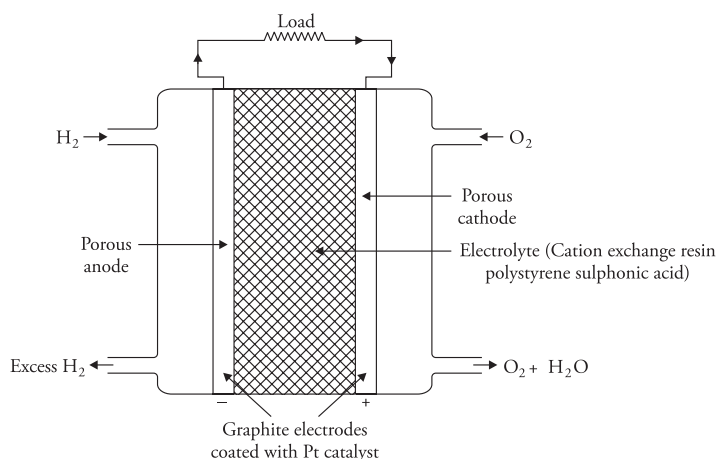
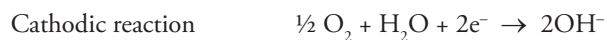


Figure 16.25 $\text{H}_2 - \text{O}_2$ fuel cell (with solid polymer electrolyte)

In another form of $\text{H}_2 - \text{O}_2$ fuel cell, alkali (aqueous 25% KOH at 200 °C) is used as an electrolyte (Fig. 16.26) and the electrodes consists of two inert porous electrodes made up of either graphite impregnated with finely divided platinum or a 75/25 alloy of palladium (Pd) with silver (Ag) or nickel (Ni). Hydrogen and oxygen are bubbled through the anode and cathode respectively. The cell reactions are



The EMF of the cell is nearly 1.23 volts.

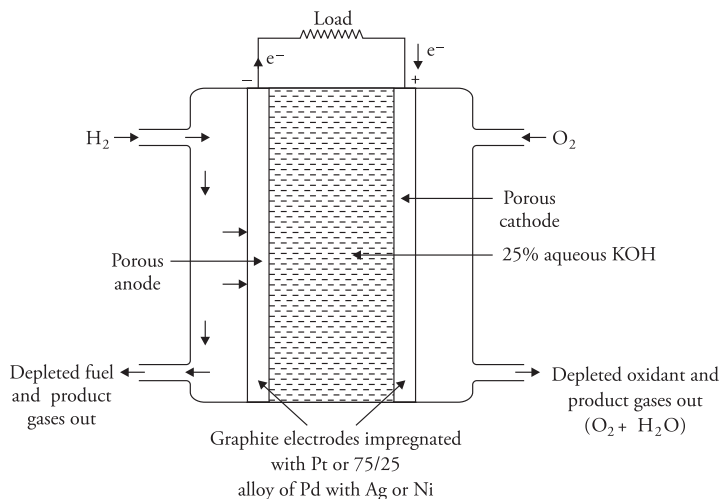
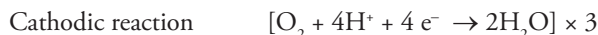
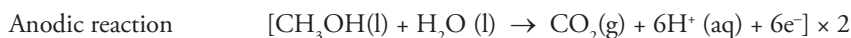


Figure 16.26 H_2 - O_2 fuel cell (with alkaline electrolyte)

Methanol-oxygen fuel cells

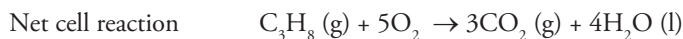
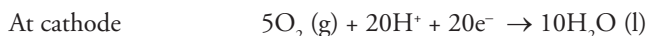
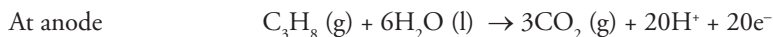
The anode is Pt, Pd or Ni and the cathode is made of Ag or Pt. Methanol and sulphuric acid are used as electrolytes.

The electrode reactions are



The cell gives a voltage of nearly 1.2 volts. It finds use in spacecraft for uninterrupted power supply and is also used by the military.

Hydrocarbon-air fuel cells Since hydrogen is an expensive gas, hydrocarbons like methane and propane are used in its place. The electrode reactions are

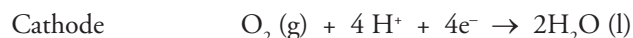


The hydrocarbons are easily oxidized even at temperature below 100°C . $E_{\text{cell}}^0 \approx 1.09$ volts. However, hydrocarbon cells require a platinum electrode which again makes them very expensive. Therefore, in practice, hydrocarbons are cracked with steam and the liberated hydrogen is separated using a Ag-Pb membrane. The separated hydrogen is then used in a $H_2 - O_2$ fuel cell.

Phosphoric acid fuel cells The electrodes are made up of porous carbon catalysed by platinum metal with a graphite cloth support (Fig. 16.27). The electrolyte used is liquid phosphoric acid which is contained in a teflon coated silicon carbide matrix placed between the electrodes. Phosphoric acid is a non-conductive electrolyte which passes hydrogen ions from the anode to the cathode. The production of hydrogen ions is increased by

- The use of platinum catalyst.
- Operating the cell at high temperature (150–200 °C)

The hydrogen ions migrate through the electrolyte and combine with oxygen or air at the cathode to form water. However, the use of platinum catalyst increases the cost of the cell. The cell reactions are as follows



The cell gives a voltage of around 0.67 V.

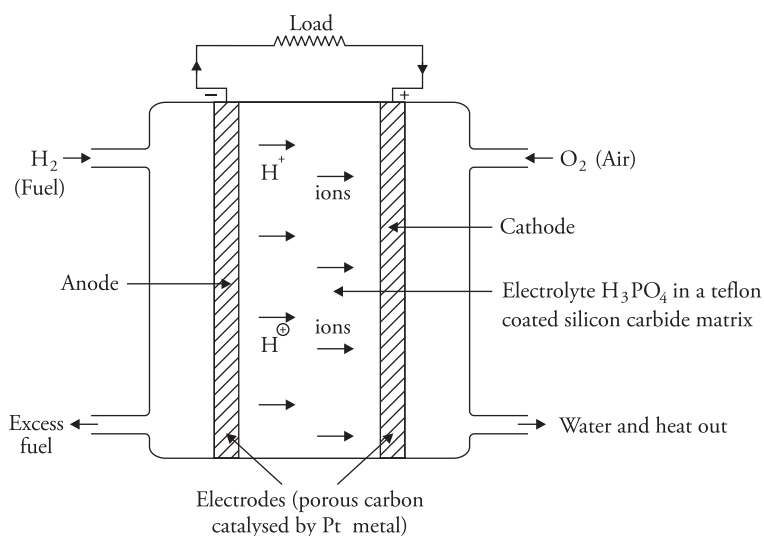


Figure 16.27 Phosphoric acid fuel cell (PAFC)

Molten carbonate fuel cells

The fuel cell consists of an anode made up of a porous structure of nickel treated with oxides to prevent sintering. The cathode is made up of lithiated sintered nickel oxide (Fig. 16.28). A molten mixture of carbonate salts like lithium carbonate Li_2CO_3 , potassium carbonate and sodium carbonate is used as an electrolyte. The electrolyte is suspended in a porous, chemically inert

ceramic lithium aluminium oxide (LiAlO_2) matrix. The cell operates at the very high temperature of 650°C to enable the carbonates to melt and to increase ionic mobility through the electrolyte. At high temperatures, natural gas, methane and steam are converted into hydrogen rich gas inside the fuel cell. The hydrogen reacts with the carbonate ions at the anode to form carbon dioxide and water. The electrons pass to the cathode through the external circuit where the oxygen from the air and CO_2 from the anode reacts with electrons to form carbonate ions. Hence, electrolyte is replenished. The cell reactions are



However, due to the use of corrosive electrolytes and high operating temperature, these cells are less durable, although, they are not easily poisoned by carbon monoxide and carbon dioxide. The cell voltages are around 0.9 V.

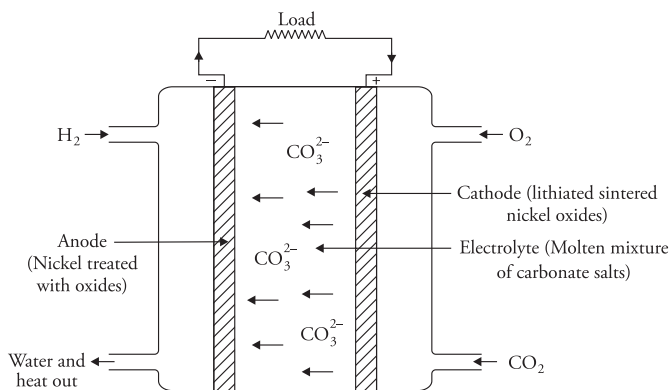
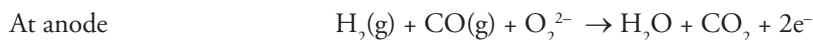


Figure 16.28 • *Molten carbonate fuel cell*

Solid oxide fuel cells (SOFC) The cells are composed entirely of solid materials. The anode is made up of nickel–zirconium oxide or nickel–yttrium oxide stabilised by zirconium oxide (Ni-YSZ). The cathode is made up of lanthanum manganate LaMnO_3 or $(\text{LaSr})\text{MnO}_3$. The electrolyte is also solid. The commonly used electrolytes are ceramic compounds (Fig. 16.29). These cells operate at very high temperatures of around 1000°C . Due to high temperature, the fuel is reformed internally. The reformate gases (hydrogen and carbon monoxide) are used as fuel, and oxygen serves as an oxidizing agent. The cell reactions are as follows:



As seen from the above reactions, unlike other fuel cells, in SOFCs, there is movement of negatively charged oxygen ions from the cathode to the anode (in other cells, positively charged hydrogen ions move from the anode to the cathode). The exhaust heat can be used to generate steam and in gas turbine engines.

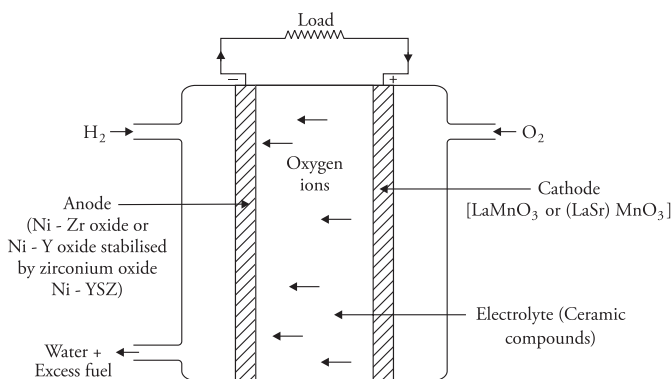


Figure 16.29 Solid oxide fuel cell

Summary

- Important relations and reactions

Parameter	Relation	Unit
Resistance	$R = \frac{V}{I}$	ohm expressed as Ω
Conductance	$G = \frac{1}{R}$	ohm ⁻¹ or mho SI unit is Siemens
Specific resistance or resistivity	$\rho = R \times \frac{a}{l}$	ohm \times cm SI unit is ohm \times m
Conductivity (Specific conductance)	$\kappa = \frac{l}{R \times a}$	ohm ⁻¹ cm ⁻¹ (Ω^{-1} cm ⁻¹) SI unit S m ⁻¹
Equivalent conductivity	$\Lambda_{eq} (\text{lambd}) = \kappa \times V = \kappa \times \frac{1000}{c}$ where c is concentration in gram equivalent per liter	ohm ⁻¹ m ² equiv ⁻¹ S cm ² equiv ⁻¹ (SI unit S m ² equiv ⁻¹)

Molar conductivity

$$\Lambda_m = \kappa \times V = \kappa \times \frac{1000}{c}$$

ohm⁻¹ cm² mol⁻¹SI units = S m² mol⁻¹

where c = concentration in moles per liter

Cell constant

$$\frac{\text{Distance between electrode}}{\text{Area of cross section}} = \frac{l}{a} \text{ or } \text{cm}^{-1}$$

$$\frac{\text{Conductivity (specific conductance)}}{\text{Observed conductance}}$$

- Representation of an electrochemical cell The anode is written on the left-hand side and the cathode on the right-hand side. The two phases are separated by a single vertical line and the two half cells are separated by two vertical lines. The concentration of species is written in front of the solution. For example, a Daniel cell can be represented as



anode has negative polarity and cathode has positive polarity.

- Each electrochemical cell is made up of two halves called the half cell. The half cell where oxidation occurs is the oxidation half cell which behaves as the anode and the half cell where reduction occurs is the reduction half cell (it behaves as the cathode).
- The electrode potential is always expressed as the reduction potential.
- EMF of a cell = electrode potential of cathode – electrode potential of anode

$$\text{EMF} = E_{\text{right}} - E_{\text{left}}$$

Electrode potential of a cell when the concentration of the electrolyte solution is unity, temperature is 298 K is called the standard electrode potential depicted by E[°].

- Nernst equation $E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]}$



$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- $\log K = \frac{nE_{\text{cell}}^0}{0.0591}$ K = equilibrium constant; E_{cell}^0 = standard electrode potential; n = number of electrons given / taken in the cell reaction

$$\Delta G = w_{\text{max}} = -nFE_{\text{cell}}$$

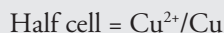
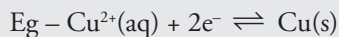
$$E = -\frac{\Delta H}{nF} + T \left(\frac{\partial E}{\partial T} \right)_p$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \text{Temperature coefficient of the cell}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_p$$

- Type of electrodes

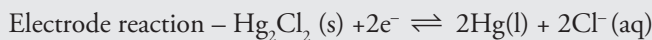
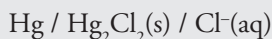
1. Metal–metal ion electrode



$$E = E_{\text{Cu}}^0 + \frac{2.303RT}{2F} \log[\text{Cu}^{2+}]$$

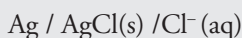
2. Metal insoluble salt electrode

- (i) Calomel electrode



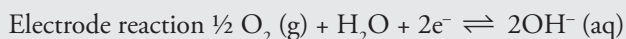
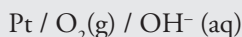
$$E = E^0 - \frac{2.303RT}{F} \log[\text{Cl}^-]$$

- (ii) Silver – silver chloride electrode

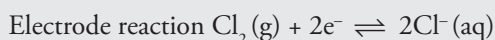
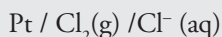


3. Gas electrode

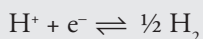
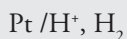
- (i) Oxygen electrode



Similarly for chlorine electrode

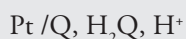


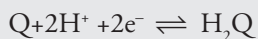
- (ii) Hydrogen electrode



4. Redox electrodes

Quinhydrone electrode:





$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[H_2Q]}{[Q][H^+]^2}$$

$$E = E^0 + \frac{2.303RT}{F} \log [H^+]$$

5. Membrane electrodes

Glass electrode

Ag, AgCl, 0.01M HCl/ glass, experimental solution / KCl, Hg₂Cl₂(s), Hg

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{1}{[H^+]}$$

6. Electrode concentration cell Pt / H₂ (p₁) / HCl / H₂ (p₂) / Pt

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{p_2}{p_1} \quad \because E^0 = 0 \text{ hence}$$

$$E = \frac{2.303RT}{nF} \log \frac{p_1}{p_2}$$

Different types of cells/batteries

Cell	Anode	Cathode	Electrolyte	Type of cell	Cell reaction
Dry cell or Leclanche cell	Zinc	Graphite	Paste of NH ₄ Cl, ZnCl ₂ , MnO ₂ with traces of acetylene black and graphite powder	Primary cell (non-chargeable)	At anode Zn(s) → Zn ²⁺ (aq) + 2e ⁻ At cathode 2MnO ₂ (s) + H ₂ O + 2e ⁻ → Mn ₂ O ₃ (s) + 2OH ⁻ Overall cell reaction Zn(s) + 2MnO ₂ (s) + H ₂ O → Zn ²⁺ (aq) + Mn ₂ O ₃ (s) + 2OH ⁻
Alkaline cell or MnO ₂ battery	Zinc	Graphite	KOH or NaOH	Primary cell (non-chargeable)	Anode Zn (s) + 2OH ⁻ (aq) → ZnO(s) + H ₂ O(l) + 2e ⁻ Cathode 2MnO ₂ + H ₂ O(l) + 2e ⁻ → Mn ₂ O ₃ (s) + 2OH ⁻ (aq) Cell reaction Zn(s) + 2MnO ₂ (s) → ZnO(s) + Mn ₂ O ₃ (s)

Nickel–cadmium battery (NiCad cell)	Spongy cadmium with cadmium hydroxide	Paste of NiO(OH) (s)	KOH (5 M)	Secondary cell (rechargeable)	<p>Anode $\text{Cd(s)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cd(OH)}_2(\text{s}) + 2\text{e}^-$</p> <p>Cathode $2\text{NiO(OH)(s)} + 2\text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow 2\text{Ni(OH)}_2(\text{s}) + 2\text{OH}^-(\text{aq})$</p> <p>Net cell reaction $\text{Cd(s)} + 2\text{NiO(OH)(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{Ni(OH)}_2(\text{s}) + \text{Cd(OH)}_2(\text{s})$</p>
Mercury battery	Zinc amalgam	Paste of mercuric oxide with some graphite	Paste of ZnO and KOH	Primary	<p>Anode $\text{Zn amalgam(s)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^-$</p> <p>Cathode $\text{HgO(s)} + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-(\text{aq})$</p> <p>Net cell reaction $\text{Zn-amalgam(s)} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + \text{Hg(l)}$</p>
Lead–acid battery	Lead grid coated with spongy lead	Lead grid coated with a paste of spongy lead and lead dioxide in the ratio 1:1	5 M H_2SO_4 (37%)	Secondary	<p>At Anode</p> $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \xrightleftharpoons[\text{charging}]{\text{discharging}} \text{PbSO}_4(\text{s}) + 2\text{e}^-$ <p>At cathode</p> $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \xrightleftharpoons[\text{charging}]{\text{discharging}} \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$ <p>Net cell reaction–</p> $\text{Pb(s)} + 2\text{SO}_4^{2-}(\text{aq}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) \xrightleftharpoons[\text{charging}]{\text{discharging}} 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

Hydrogen–oxygen fuel cell	Both the electrodes are made of porous screens of graphite coated with a layer of platinum catalyst		Polymeric ion exchange resin (polystyrene sulphonic acid or polymeric forms of perfluoro-sulphonic acid) or aqueous KOH 25%	Fuel cell	Anodic reaction $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ Cathodic reaction $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ Overall cell reaction $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$
Methanol–oxygen fuel cell	Pt, Pd or Ni	Ag or Pt	Methanol and sulphuric acid	Fuel cell	Anodic reaction $\text{CH}_3\text{OH}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{CO}_2(\text{g}) + 6\text{H}^+(\text{aq}) + 6\text{e}^- \times 2$ Cathodic reaction $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ $\times 3$ Overall cell reaction $2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$
Phosphoric acid fuel cell	Both the electrodes are made of porous carbon, catalysed by Pt metal with a graphite cloth support		Liquid phosphoric acid contained in a teflon coated silicon carbide matrix	Fuel cell	Anode $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$ Cathode $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$ Net cell reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
Molten carbonate fuel cell	Porous structure of Ni coated with oxides	Lithiated sintered nickel oxide	Molten mixture of carbonate salts like Li_2CO_3 , K_2CO_3 , Na_2CO_3 , electrolyte suspended in ceramic lithium aluminium oxide (LiAlO_2) matrix	Fuel cell	Anode reaction $\text{CO}_3^{2-} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ Cathode reaction $\text{CO}_2 + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$ Overall cell reaction $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$
Solid oxide fuel cell (SOFC)	Nickel zirconium oxide or nickel yttrium oxide stabilised on zirconium oxide (NiYSZ)	Lanthanum manganate LaMnO_3 or (LaSr) MnO_3	Electrolyte is a solid. Generally ceramic compounds are used as electrolytes	Fuel cell The cell operates at very high temperature of around 1000 °C	At anode $\text{H}_2(\text{g}) + \text{CO}(\text{g}) + \text{O}_2^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ At Cathode $\text{O}_2 + 2\text{e}^- \rightarrow \text{O}_2^{2-}$ Overall cell reaction $\text{O}_2 + \text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{CO}_2$
Zn–air battery	Zinc plates	Perforated carbon plate treated with water repellents	NaOH or KOH (5 M)	They have properties of both fuel cells and batteries	At anode $2\text{Zn}(\text{s}) + 4\text{OH}^-(\text{aq}) \rightarrow 2\text{ZnO}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$ At cathode $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ Overall cell reaction $2\text{Zn}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s})$

Nickel metal hydride batteries (NiMH)	Nickel foil or grid coated with hydrogen absorbing alloys like zirconium hydride ZrH_2 , vanadium hydride VH_2 , titanium hydride TiH_2 absorbed on an alloy of $LaNi_5$ and $TiAl$	Nickel foil coated with nickel hydroxide and nickel oxyhydroxide; polypropylene is used as a separator to separate the anode and the cathode	KOH (5 M)	Rechargeable batteries	<p>At anode</p> $MH(s) + OH^-(aq) \xrightleftharpoons[\text{charging}]{\text{discharging}} M(s) + H_2O(l) + e^-$ <p>MH is metal hydride and M is the metal</p> <p>At cathode $NiO(OH)(s) + e^- + H_2O(l) \xrightleftharpoons[\text{charging}]{\text{discharging}} Ni(OH)_2(aq) + OH^-(aq)$</p> <p>Net cell reaction</p> $MH(s) + NiO(OH)(s) \xrightleftharpoons[\text{charging}]{\text{discharging}} Ni(OH)_2(aq) + M(s)$
Lithium MnO_2 battery	Lithium metal or lithium compounds	Specially treated MnO_2 crystals	Lithium salt solution in propylene carbonate and dimethoxy salts	Primary (non-rechargeable)	<p>At anode $Li \rightarrow Li^+ + e^-$</p> <p>At cathode $Mn(IV)O_2 + Li^+ + e^- \rightarrow Li^+Mn(III)O_2$</p> <p>The net cell reaction</p> $Mn(IV)O_2 + Li \rightarrow Li^+Mn(III)O_2$

Review Questions

- What is conductivity (specific conductance), equivalent conductivity and molar conductance? Give the relation between them. Explain the effect of dilution on them.
- State and explain the Kohlrausch's law. How does this law help in the determination of the equivalent conductivity at infinite dilution of a weak electrolyte?
- What is the principle of conductometric titrations? Give its advantages. Discuss the conductometric titrations in the following cases.
 - Strong acid and strong base
 - Strong acid and weak base
 - Weak acid and strong base

- (iv) Weak acid and weak base
 - (v) Precipitation reactions.
4. What is single electrode potential? Explain its origin. Explain the following.
 - (i) Notations and sign conventions of electrochemical cells.
 - (ii) Functions of a salt bridge
 - (iii) Different types of reversible electrodes
 - (iv) Construction and working of a calomel electrode
 - (v) Factors affecting conductance of an electrolytic solution
 5. What are reference electrodes? Describe the construction and working of a glass electrode. How can it be used for the determination of pH of a solution?
 6. What do you understand by a concentration cell? Derive an expression for the EMF of the following cell.
 $\text{Ag (Hg)} c_1 / \text{AgNO}_3(\text{soln}) / \text{Ag(Hg)} c_2$
Explain the various applications of concentration cells.
 7. What is an electrochemical series? Explain the various applications of the electrochemical series.
 8. Derive the Nernst equation. How does it explain the dependence of the electrode potential on concentration of the electrolyte solution? How can you determine the equilibrium constant of a reaction using Nernst equation?
 9. What is a battery? Explain the different types of batteries taking a suitable example of each type.
 10. What is a primary cell? Explain the dry battery or the Leclanche cell.
 11. What are secondary cells? Explain the construction and working of lead–acid battery. Write down the reactions taking place during charging and discharging of the battery.
 12. What is an alkaline battery? Explain taking suitable examples.
 13. Explain the construction and working of a nickel– cadmium battery. What are the reactions in each half of the cell?
 14. What is a fuel cell? Explain the underlying principle taking the example of an $\text{H}_2\text{--O}_2$ fuel cell with solid polymer electrolyte and an alkaline electrolyte.
 15. With the help of suitable diagrams, explain the following:
 - (i) Phosphoric acid fuel cell
 - (ii) Molten carbonate fuel cell
 - (iii) Solid oxide fuel cell
 - (iv) Zinc–air battery
 - (v) Nickel metal hydride batteries (NiMH batteries)
 16. What is a reserve battery? Explain with the help of a suitable example.

Multiple Choice Questions

- On dilution specific conductance of an electrolyte
 - Increases
 - Decreases
 - First increases then decreases
 - Neither increases nor decreases
- The unit of equivalent conductivity is
 - Mho
 - $\text{Ohm}^{-1} \text{cm}^{-1}$
 - $\text{Ohm}^{-1} \text{cm}^{-1} \text{equiv}^{-1}$
 - $\text{Ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$
- Cell constant is defined as
 - Ratio of distance between electrodes and their area of cross-section
 - Ratio of specific conductance to the observed conductance
 - Both (a) and (b)
 - None of the above
- Which of the following statement is incorrect about an electrochemical cell?
 - Oxidation occurs at the anode and reduction occurs at the cathode.
 - Chemical energy converts into electrical energy and vice versa
 - Cell can work indefinitely
 - Salt bridge reduces the liquid junction potential of the cell
- The EMF of an electrochemical cell is given by the relation
 - $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
 - $E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$
 - $E_{\text{cell}} = E_{\text{left}} - E_{\text{right}}$
 - None of the above
- Given

$$\text{Zn}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Zn} \quad E^{\circ} = -0.76 \text{ V}$$

$$\text{Fe}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Fe} \quad E^{\circ} = -0.44 \text{ V}$$
 The cell reaction is

$$\text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe}$$
 The standard potential of the above cell will be
 - 1.2 V
 - 0.32 V
 - +0.32 V
 - 1.20 V
- For the electrode reaction

$$\text{M}^{n+}(\text{aq}) + n\text{e}^{-} \rightarrow \text{M}(\text{s})$$
 The Nernst equation is –
 - $E = E^{\circ} + \frac{RT}{nF} \log \left[\frac{1}{\text{M}^{n+}} \right]$
 - $E = E^{\circ} + \frac{RT}{nF} \log \left[\text{M}^{n+} \right]$
 - $E = E^{\circ} - \frac{RT}{nF} \log \left[\text{M}^{n+} \right]$
 - $E = E^{\circ} + \frac{RT}{nF} \ln \left[\text{M}^{n+} \right]$
- The relation between E°_{cell} and ΔG° is–
 - $\Delta G^{\circ} = nFE^{\circ}_{\text{cell}}$
 - $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$
 - $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$
 - $\Delta G^{\circ} = nFE^{\circ}_{\text{cell}} = 0$

9. If the specific conductance of a solution of concentration c gram equiv per liter is κ , then its equivalent conductivity is

(a) $\frac{1000 \times \kappa}{c}$ (b) $\frac{\kappa \times c}{1000}$
(c) $\frac{1000}{\kappa \times c}$ (d) $\frac{c}{1000 \times \kappa}$

10. EMF of an electrolyte concentration cell is given by

(a) $E = \frac{2.303}{n} \log \frac{c_2}{c_1}$ (b) $E = \frac{RT}{nF} \log \frac{c_1}{c_2}$
(c) $E = \frac{0.0591}{n} \log \frac{c_2}{c_1}$ (d) $E = \frac{0.0591}{n} \log \frac{c_1}{c_2}$

11. The cell reaction will be spontaneous if its EMF is

- (a) Positive (b) Negative
(c) Zero (d) Fixed

12. The entropy change ΔS of a cell reaction can be obtained by the relation

(a) $\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p$ (b) $\Delta S = n \left(\frac{\partial E}{\partial T} \right)_p$
(c) $\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_V$ (d) $\Delta S = nF \left(\frac{\partial E}{\partial V} \right)_T$

13. Glass electrode is an example of

- (a) Redox electrode (b) Ion selective electrode
(c) Metal insoluble salt electrode (d) Gas electrode

14. A battery that remains in the inactive state and is activated immediately before use is the

- (a) Primary cell (b) Secondary cell
(c) Reserve battery (d) Fuel cell

15. In a Leclanche cell, the anode is

- (a) Graphite rod (b) FeO and Fe(OH)₃
(c) Zinc container (d) MnO₂ + C

16. Which of the following is not an alkaline battery?

- (a) Nickel cadmium battery (b) Mercury battery
(c) Zinc–air battery (d) Lead acid battery

17. In a solid oxide fuel cell, the electrolyte is

- (a) NaOH or KOH (b) Ceramic compounds
(c) H₂SO₄ (d) Liquid phosphoric acid

18. Which of the following is not a secondary cell?
 (a) Lithium– MnO_2 battery (b) Lead–acid battery
 (c) Nickel–cadmium battery (d) Nickel metal hydride battery
19. The specific conductance of a solution is $0.3568 \text{ ohm}^{-1}\text{cm}^{-1}$. When placed in a cell, the conductance is 0.0268 ohm^{-1} . The cell constant is
 (a) 1.331 cm^{-1} (b) 13.31 cm^{-1}
 (c) 0.665 cm^{-1} (d) 6.65 cm^{-1}
20. According to Kohlrausch's law, the limiting value of molar conductivity of an electrolyte A_2B is
 (a) $\lambda_A^\infty + \lambda_B^\infty$ (b) $\lambda_A^\infty - \lambda_B^\infty$
 (c) $\lambda_A^\infty + \frac{1}{2}\lambda_B^\infty$ (d) $2\lambda_A^\infty + \lambda_B^\infty$

Solution

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (d) | 3 (c) | 4 (c) | 5 (a) | 6 (c) | 7 (d) | 8 (c) |
| 9 (a) | 10 (c) | 11 (a) | 12 (a) | 13 (b) | 14 (c) | 15 (c) | 16 (d) |
| 17 (b) | 18 (a) | 19 (b) | 20 (d) | | | | |

Chapter 17

SPECTROSCOPY

17.1 Introduction

Spectroscopy is the branch of science which deals with the study of the interaction of electromagnetic radiation with matter. It is the most powerful tool available for the study of structures of atoms and molecules. There are several spectroscopic techniques that help in investigating various aspects of atomic and molecular structure. In this chapter, we will discuss the common spectroscopic techniques like electronic spectroscopy (which includes UV–visible), infrared spectroscopy (IR), rotational, microwave, nuclear magnetic resonance (NMR) and Raman spectroscopy. The chapter deals with the principles, experimental techniques and applications of the various spectroscopic methods. However, before starting it is essential to discuss some basic fundamentals of spectroscopy.

17.2 Basic Terms and Principles of Spectroscopy

Electromagnetic radiations

Electromagnetic radiation is a form of radiant energy which has both particle as well as wave nature. In vacuum, it normally travels in a straight line with the speed of light (3×10^8 m/s). It has both electric and magnetic field components, which are coplanar and oscillate perpendicular to each other and perpendicular to the direction of wave propagation (Fig. 17.1).

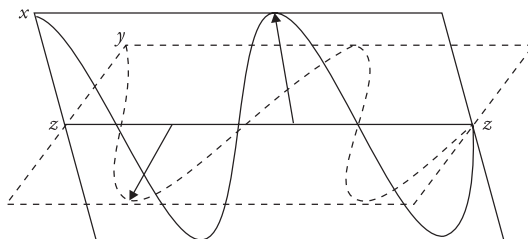


Figure 17.1 Planes of electromagnetic waves

Properties of electromagnetic radiations

The properties of electromagnetic radiation can be described easily by ascribing wave nature to these radiations.

- (a) **Wavelength** It is denoted by λ (lambda) and is defined as the distance between two adjacent crests (C–C) or troughs (T–T) in a particular wave (Fig. 17.2). It can be expressed in centimeters. The other units for expressing wavelength are given below.

(i) Angstrom (\AA) $1 \text{\AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$

(ii) Nanometer (nm) or millimicron ($\text{m}\mu$)

$$1 \text{ nm} = 1 \text{ m}\mu = 10^{-7} \text{ cm} = 10^{-9} \text{ m}$$

(iii) Micron (μ) $1\mu = 10^{-4} \text{ cm} = 10^{-6} \text{ m}$

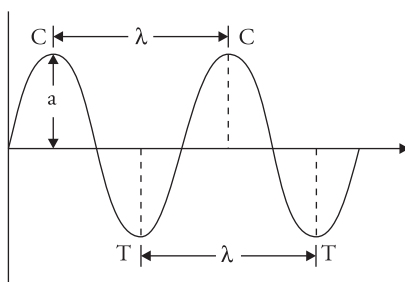


Figure 17.2 Properties of electromagnetic radiations

The wavelength of visible light ranges from 3800 \AA (violet end) to 7600 \AA (red end).

- (b) **Frequency** It is denoted by ν (nu) and is defined as the number of waves which can pass through a point in one second. Frequency is expressed in cycles per second or Hertz (Hz) where $1 \text{ Hz} = 1 \text{ cycle/s}$.

$$\text{Frequency } (\nu) = \frac{c}{\lambda}$$

where c = velocity of electromagnetic radiation in $\text{cm/s} = 2.998 \times 10^{10} \text{ cm/s}$.

λ = wavelength.

We know that the wavelength of visible light is 3800–7600 \AA . The corresponding frequency can be calculated as follows.

(i) When $\lambda = 3800 \text{\AA} = 3800 \times 10^{-8} \text{ cm}$,

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10} \text{ cm s}^{-1}}{3800 \times 10^{-8} \text{ cm}}$$

$$= 7.88 \times 10^{14} \text{ s}^{-1} = 7.88 \times 10^{14} \text{ Hz} = 7.88 \times 10^8 \text{ MHz}$$

(ii) When $\lambda = 7600 \text{ \AA} = 7600 \times 10^{-8} \text{ cm}$.

$$\nu = \frac{2.998 \times 10^{10} \text{ cm s}^{-1}}{7600 \times 10^{-8} \text{ cm}} = 3.94 \times 10^{14} \text{ s}^{-1}$$

$$= 3.94 \times 10^8 \text{ MHz}$$

Thus, the frequency range of visible light is $7.88 \times 10^8 \text{ MHz}$ to $3.94 \times 10^8 \text{ MHz}$.

- (c) **Velocity** Velocity of a wave is denoted by c and is defined as the distance travelled by a wave in one second. Electromagnetic radiations travel with the speed of light, hence the value of c is $2.998 \times 10^8 \text{ cm/s}$ or 18600 miles per second.
- (d) **Wave number** It is denoted by $\bar{\nu}$ (nu bar) and is defined as the total number of waves in a length of one centimetre. Wave number is the reciprocal of wavelength and is expressed in per centimetre or cm^{-1} .

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}}$$

- (e) **Energy** Energy of a wave can be calculated by applying the Planck relation.

$$E = h\nu = \frac{hc}{\lambda}$$

where h = Planck constant = 6.626×10^{-34} Joule seconds

ν = frequency of radiation in cycles/s

λ = wavelength in meters

It should be noted that the energy of a wave is directly proportional to its frequency and inversely proportional to its wavelength.

Solved Examples

- Calculate the energy associated with a radiation having wavelength 3000 \AA . Give the answer in kcal mol^{-1} and also in kJ mol^{-1} .

Solution

$$\lambda = 3000 \text{ \AA} = 3000 \times 10^{-8} \text{ cm}$$

$$E = h \cdot \frac{c}{\lambda}$$

$$= \frac{6.628 \times 10^{-27} \text{ erg s} \times 2.998 \times 10^{10} \text{ cm s}^{-1}}{3000 \times 10^{-8} \text{ cm}} = 6.6236 \times 10^{-12} \text{ ergs}$$

$$= \frac{6.6236 \times 10^{-12} \times 6.023 \times 10^{23}}{4.18 \times 10^{10}} \because 1 \text{ mole} = 6.023 \times 10^{23} \text{ and } 4.187 \times 10^7 \times 10^3 \text{ erg} = 1 \text{ kcal}$$

$$= 95.4 \text{ kcal mol}^{-1}$$

Also 1 kcal = 4.184 kJ

$$\therefore E = 95.4 \times 4.184 = 399.15 \text{ kJ mole}^{-1}$$

2. Calculate the wave number of a radiation whose wavelength is 2.5μ .

Solution

$$\lambda = 2.5 \mu = 2.5 \times 10^{-4} \text{ cm}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.5 \times 10^{-4} \text{ cm}} = 4000 \text{ cm}^{-1}$$

3. Calculate the frequency of radiation whose wavelength is 400 nm. Express this wavelength in wave number.

Solution

$$\lambda = 400 \text{ nm} = 400 \times 10^{-7} \text{ cm}$$

$$\text{Frequency } \nu = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm/s}}{400 \times 10^{-7} \text{ cm}} = 7.5 \times 10^{14} \text{ cycles/s}$$

$$\text{Wave number } \bar{\nu} = \frac{1}{\lambda(\text{cm})} = \frac{1}{400 \times 10^{-7} \text{ cm}} = 25000 \text{ cm}^{-1}$$

Practice Problems

- The frequency of a radiation is found to be $5.09 \times 10^{14} \text{ s}^{-1}$. Calculate the wavelength in nanometres. (Given $c = 3 \times 10^8 \text{ m/s}$) [Ans 589.4 nm]
- Calculate the wave number of the radiation if the frequency is $2.06 \times 10^{14} \text{ Hertz}$. (Given $c = 3 \times 10^{10} \text{ cm/s}$) [Ans 6866.6 cm^{-1}]

Electromagnetic spectrum

An electromagnetic spectrum is obtained when all types of electromagnetic radiations are arranged in the order of increasing wavelength or decreasing frequencies (Fig. 17.3).

Visible light lies in the wavelength range 3800–7600 Å. The region of 3800 Å corresponds to *violet colour* and that of 7600 Å corresponds to *red colour*. If the wavelength is less than 3800 Å, the radiation is called ultraviolet radiation and if it is greater than 7600 Å, it is called infrared radiations. Both infrared and ultraviolet radiations are not visible to the human eye. Beyond infrared region, on the side of increasing wavelength are microwaves. Beyond microwaves, lie the radio waves which have the highest wavelength.

The arrangement of different types of electromagnetic radiation in increasing order of their wavelength is

Cosmic rays < γ rays < X rays < Ultraviolet rays < Visible rays < Infrared rays < Microwaves < Radiowaves

Since $\nu = \frac{c}{\lambda}$, increasing wavelength means decreasing frequency. Thus, cosmic rays have the highest frequencies and radio waves, the least frequencies.

All types of electromagnetic radiations travel with the same speed, the velocity of light, but their wavelength (or frequency) differ from each other. Radio waves are least energetic (maximum wavelength, minimum frequency) and cosmic rays have maximum energy (minimum wavelength

$$E = \frac{hc}{\lambda})$$

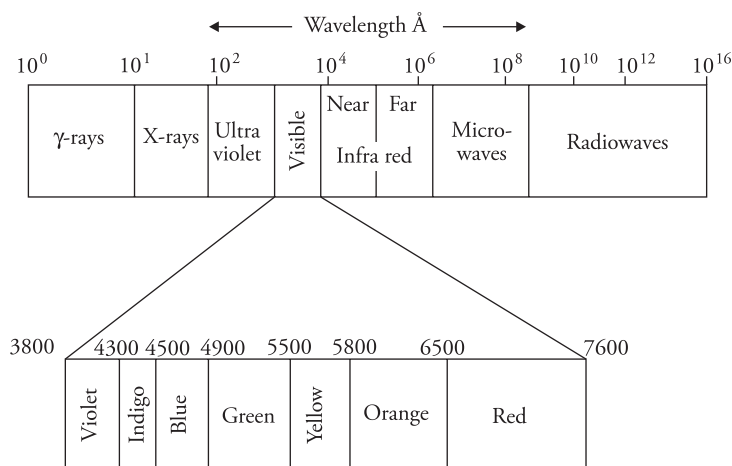


Figure 17.3 Electromagnetic spectrum

Origin of electronic spectra

When a sample of molecules is exposed to electromagnetic radiation, the electric field of the radiation interacts with the electrical charges (electrons and nuclei) of the molecule. Quantum mechanics deals with such interactions and the quantum mechanical treatment shows that when a molecule in state E_1 is irradiated, it may absorb a photon of frequency ν and may get promoted to a higher energy state E_2 if the frequency of radiation satisfies the condition $E_2 - E_1 = h\nu$. Similarly, a photon will be emitted only if the above mentioned condition is satisfied.

$$\Delta E \propto \nu \text{ or } \Delta E = h\nu$$

where h is the Planck constant. It has a value of 6.63×10^{-34} J s. The energy emitted or absorbed by a body will be some whole number multiple of a quantum, that is,

$$E = nh\nu$$

where n is an integer such as 1, 2, 3. Hence, a body can emit or absorb energy equal to $h\nu$, $2h\nu$, $3h\nu$... but not $1.6h\nu$, $2.2h\nu$... or any other fractional value.

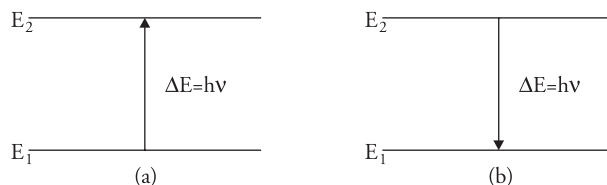


Figure 17.4 Energy transition for (a) absorption (b) emission

The frequency of absorbed or emitted radiation is given (Fig. 17.4) by

$$\nu = \frac{\Delta E}{h} \text{ Hz}$$

The energy change or frequency of electromagnetic radiation emitted or absorbed can be recorded in the form of a spectrum with the help of an instrument called spectrophotometer. A spectrum is a plot of the absorbance or transmittance of radiation against energy.

There are different types of spectra. They are explained below.

- (i) **Continuous spectrum** When white light passes through a prism, it splits into different colours. These colours merge into one another without any discontinuity. Such a spectrum is called a continuous spectrum. A continuous spectrum can be obtained from light emitted by some incandescent substances.
- (ii) **Emission spectrum** When there is transition from a higher energy level to a lower energy level (Fig. 17.4b), energy is emitted out and the spectrum thus obtained is called an emission spectrum.

An emission spectra is obtained by heating the substance and then passing the emitted radiation through a prism.

- (iii) **Absorption spectrum**

When there is transition from a lower energy state to a higher energy state, the energy absorbed will be equal to the energy difference ΔE . The spectrum thus obtained is called an absorption spectrum.

When a continuous electromagnetic radiation (say, white light) is allowed to pass through a gas or solution of some salt and then analysed, we obtain dark lines in the otherwise continuous

spectrum. The dark lines indicate that the radiations of corresponding wavelengths have been absorbed by the substance from white light. Such a spectrum containing dark lines due to the absorption of light is known as an absorption spectrum.

Emission or absorption spectrum can be of two types.

(i) Atomic spectra (ii) Molecular spectra

Atomic spectra

When atoms interact with electromagnetic radiation, the spectrum obtained is called an atomic spectrum. The transition of electrons takes place between the electronic energy levels of the atom. The spectra are obtained as sharp lines. These lines are characteristic of the atom, hence, line spectra are also regarded as finger prints of the atoms.

Molecular spectra

Molecular spectroscopy deals with the interaction of electromagnetic radiations with molecules. In the spectra of molecules, in addition to electronic levels, transitions also occur between rotational and vibrational levels.

In this chapter, we will discuss molecular spectroscopy.

Types of energy changes

A number of energy states are possible in molecules. The total energy is the sum of the translational, rotational, vibrational and electronic energy.

$$E_{\text{total}} = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

Moreover $E_{\text{electronic}} \gg E_{\text{vibrational}} \gg E_{\text{rotational}} \gg E_{\text{translational}}$

Since translational energy is negligibly small, and is not involved in molecular spectra, hence we can write the Born–Oppenheimer approximation as $E_{\text{total}} = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$.

When the molecule is excited, it absorbs energy and electrons transit from an orbit of lower energy to an orbit of higher energy. The frequency of spectral lines is determined by the difference in the two energy levels. Now if electronic transition was the only mode in which a molecule would absorb or emit energy, then molecular spectra would have been a line spectrum similar to that of atoms. However, molecular spectrum is a band spectrum. This is because apart from electronic transition, rotational and vibrational changes also occur within the molecule. These rotational and vibrational motions are also quantised and are superimposed on the kinetic motion of the molecule. Thus, there are three types of changes in a molecule (Fig. 17.5).

1. Energy change due to transition of an electron from one orbit to another.
2. Energy change due to rotation of the molecule.
3. Energy change due to vibration of atoms of the molecule relative to one another.

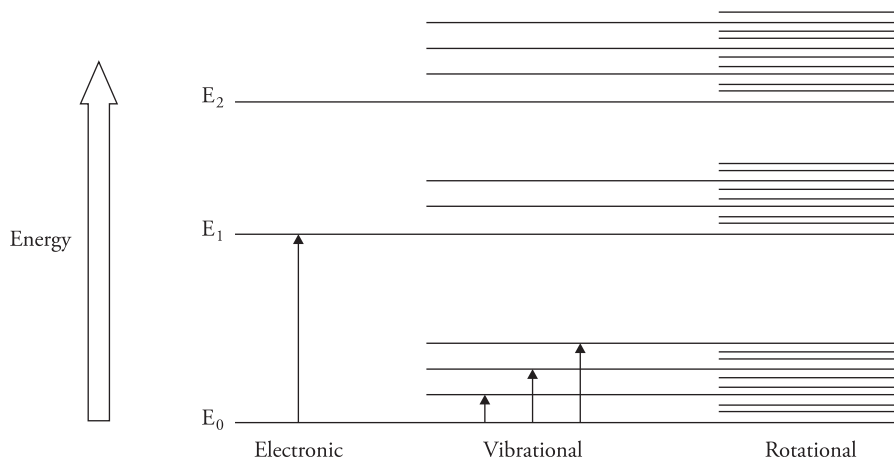


Figure 17.5 Different types of transitions in molecules

Types of molecular spectra

Different regions of the electromagnetic spectrum have different effects on interaction with matter. Molecular spectra are classified on the basis of the region of electromagnetic spectrum in which the transitions or changes take place. They are summarized in Table 17.1.

Table 17.1 Various types of molecular spectra and their origin

S. No.	Spectral region	Wavelength	Type of transition	Spectroscopy
1	Microwave	$1 - 100 \text{ cm}^{-1}$	Between rotational energy levels	Microwave spectroscopy (rotational spectroscopy)
2	Infrared	$667 - 4000 \text{ cm}^{-1}$	Between vibrational energy levels	Infrared spectroscopy (vibrational and vibrational–rotational spectroscopy)
3	Visible and ultraviolet	$12500 - 25000 \text{ cm}^{-1}$ (visible) $25000 - 70,000 \text{ cm}^{-1}$ (UV)	Between electronic energy levels	Ultraviolet–visible spectroscopy (electronic spectroscopy)
4	Radio frequency	$< 1 \text{ cm}^{-1}$ region	Between the nuclear spin energy of the molecules in the applied magnetic field	Nuclear magnetic resonance spectroscopy
5	Microwave region	$1 - 100 \text{ cm}^{-1}$ ($2 - 9.6 \text{ GHz}$)	Between the electron spin energy of the molecules in the applied magnetic field	Electron spin resonance spectroscopy

General instrumentation

The instrument used to measure the absorption or emission of electromagnetic radiation by the sample under examination is called spectrometer. Spectrometers are of different types but the basic

design is similar. The individual components of the instrument might be different according to the optical region to be studied. For example, sample containers in ultraviolet spectroscopy are made of glass or quartz, whereas sample containers used in infrared spectroscopy are made up of NaCl and KBr.

There are five basic components.

1. Source of electromagnetic radiation.
 2. Monochromator
 3. Sample containers for sample and solvent
 4. Detector unit
 5. Signal indicator or recording unit.
1. **Source of electromagnetic radiation** Incident light of required wavelength is provided by different sources for different spectroscopic techniques. The light sources used are summarized in Table 17.2.

Table 17.2 Various light sources

Spectral region	Light source
Visible spectroscopy	Incandescent tungsten filament lamp
Ultraviolet spectroscopy	Hydrogen discharge lamps and deuterium discharge lamps
Infrared spectroscopy	Electrically heated ($\sim 1500^\circ\text{C}$) rods of <ul style="list-style-type: none"> • Nernst glower (sintered mixture of oxides of Zr, Y, Er, etc.) • Globar (silicon carbide) • Ceramic element For near infrared, a tungsten filament lamp is satisfactory.
Microwave spectroscopy	Klystron tube which is a specially developed electron tube in which electrons generate electromagnetic radiations

2. **Monochromator** A monochromator is used to convert polychromatic radiation into monochromatic radiations. It is a device that resolves radiations into its component wavelengths and then isolates the desired portion of the spectrum.
A monochromator unit consists of an entrance slit, focussing lens, dispersing device (prisms and gratings), filters and an exit slit.
3. **Sample containers** The sample is placed in sample containers called cuvettes or cells. A cuvette or cell must be transparent in the spectral region of interest. For ultraviolet region, the cell is made up of quartz or fused silica. If glass is used, the cell is useful only in the visible region. The sample containers used in infrared spectroscopy are generally made up of NaCl or KBr.
4. **Detector unit** The function of the detector is to absorb the energy of the photons and convert it into a measurable quantity such as an electric current. A detector will be useful if
 - it responds to radiant energy over a broad wavelength range
 - it responds rapidly to radiation and is sensitive to low levels of radiant power.

The detectors generally produce an electric signal that can be readily amplified and the signal produced is proportional to the power of the beam striking it.

In UV–visible spectroscopy, photocells or photomultipliers are used as detectors (they detect photons). In the infrared region, thermocouples are used (they detect heat), whereas in the microwave region, the detector is a crystal rectifier.

5. **Amplification and recording unit** The function of the amplifier is to amplify a signal so that it can be measured. An amplifier takes an input signal from the circuit and through electronic operations produces an amplified output signal which is recorded on a graph or on the computer monitor. Most recording spectrophotometers record wavelength versus absorbance. The absorbance A or optical density is given by

$$A = \log \frac{I_0}{I}$$

where I_0 is the intensity of incident light and I is the intensity of transmitted light. A schematic representation of a spectrometer is given in Fig. 17.6.

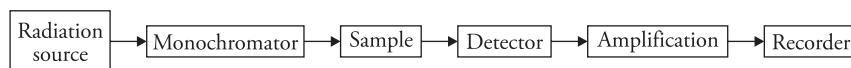


Figure 17.6 Block diagram of a spectrometer

17.3 Electronic (UV–Visible) Spectroscopy

Introduction

Electronic spectroscopy is the branch of spectroscopy that deals with the transitions of electrons between the electronic energy levels. The energy difference between the energy levels is such that the electronic spectra are observed in the UV–visible region of the electromagnetic spectrum extending from 200 to 760 nm (UV region 200–380 nm and visible region 380–760 nm). Hence electronic spectroscopy is termed as the UV–visible spectroscopy.

UV–visible spectroscopy is also called electronic spectroscopy as it involves the promotion of electrons (σ , π , n) from the ground state to higher energy states. Ultraviolet spectroscopy is used to measure the number of conjugated double bonds, differentiate between conjugated and non-conjugated systems. It also measures aromatic conjugation within the molecules.

Since energy levels in the molecule are quantised, when radiation of a fixed frequency falls on a molecule, it absorbs energy and the electrons are promoted to higher energy states. Thus, the intensity of the light ray decreases after passing through the sample. A record of the amount of light absorbed by the sample as a function of the wavelength of light in $m\mu$ or nm units is called the absorption spectrum, which generally consists of absorption bands.

Laws of absorption

Two fundamental laws govern the absorption of light by molecules. These are

1. Lambert's law

2. Beer's law

Lambert's law It states that when a beam of monochromatic light passes through a homogenous absorbing medium, the rate of decrease of intensity of radiation with thickness of absorbing medium is proportional to the intensity of the incident radiation. Mathematically,

$$\frac{-dI}{dx} \propto I \quad \text{or} \quad \frac{-dI}{dx} = kI \quad (1)$$

where k = proportionality constant

I = intensity of incident radiation

dI = infinitesimally small decrease in the intensity of radiation on passing through an infinitesimally small thickness, dx of the absorbing medium. The negative sign on the left-hand side indicates that I decreases as x increases. Equation (1) can be written as

$$\frac{-dI}{I} = k \, dx \quad (2)$$

Equation (2) can be integrated with the boundary condition that $I = I_0$ at $x = 0$ and $I = I$ at $x = x$, as,

$$\int_{I_0}^I \frac{-dI}{I} = \int_0^x k \, dx$$

$$\log_e \frac{I_0}{I} = kx$$

$$\text{or, } 2.303 \log_{10} \frac{I_0}{I} = kx$$

$$\text{or } \log_{10} \frac{I_0}{I} = \frac{kx}{2.303}$$

$$\text{or, } \log_{10} \frac{I_0}{I} = \epsilon x \quad \epsilon = \text{Absorption coefficient}$$

$$\text{or, } \log_{10} \frac{I_0}{I} = A \quad A = \text{Absorbance or optical density}$$

I_0 is the intensity of radiation before entering the absorbing medium (i.e., when $x = 0$) and I is the intensity when the beam has travelled the thickness x of the absorbing material. The term $\log_{10} \frac{I_0}{I}$ is known as absorbance or optical density and is denoted by A .

Alternatively, Lambert's law can be stated as

When a parallel beam of monochromatic light enters perpendicularly into a homogenous absorbing medium, the absorbance is directly proportional to the length of the path traversed by the beam.

Beer's law If the absorbing material is in the form of a solution, then the relationship between the intensities of incident and transmitted light is given by Beer's law.

According to this law, *when a parallel beam of monochromatic light enters perpendicularly into a dilute solution, the absorbance is directly proportional to the concentration of the solution.* Mathematically,

$$A = \log_{10} \frac{I_0}{I} = k'c$$

where k' is a constant and c is the concentration of the solution.

Beer–Lambert law It is the combined form of Beer's law and Lambert's law. According to this law *when a beam of monochromatic light is passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as to the concentration of the solution*

If a monochromatic light of intensity I passes through a solution of molar concentration c and the length of the path is x cm, then the mathematical form of Beer–Lambert's law is

$$A = \log \frac{I_0}{I} = \epsilon cx$$

Units

$$\epsilon = \text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

$$A = \text{dimensionless}$$

$$c = \text{mol dm}^{-3}$$

$$x = \text{cm}$$

where ϵ is a constant called the **molar absorption coefficient or molar absorptivity**. If $c = 1$ and $x = 1$, then

$$\text{Extinction } A = \epsilon$$

Thus, **molar absorption coefficient** (formally, the **molar extinction coefficient**) can be defined as the extinction due to a 1-cm-thick layer of solution whose molar concentration is unity. It is characteristic of a compound provided the wavelength of light and temperature are kept constant.

Transmittance If T is the transmittance of a solution, then it is defined as

$$T = \log \frac{I}{I_0}$$

$$\text{or } T = -\epsilon cb$$

Transmittance is the reciprocal of absorbance.

Instrumentation

A spectrophotometer (which is regarded as a combination of a spectrometer and a photometer) is used to detect the percentage transmittance or absorbance of light radiation when light of a certain intensity or frequency range is passed through the sample. The instrument compares the intensity of the transmitted light with that of the incident light. It consists of the following.

- (i) **An intense source of radiant energy** The most common source of visible radiation is an incandescent tungsten filament lamp. Hydrogen/deuterium discharge lamps are used for the ultraviolet region.
- (ii) **A filter or monochromator** to isolate the desired wavelength region.
- (iii) **Sample holder** A pair of cuvettes, one for the sample and the other for the blank or reference solution is used. For work in the ultraviolet region, the cuvette must be made of quartz whereas glass cuvettes can be used for visible region. The thickness of the cuvette is generally 1, 2 and 5 cm.
- (iv) **Radiation detectors** These are photoelectric devices which convert radiant energy into electric signals.

Ordinary spectrometers cover a range 220–800 nm. Spectroscopic techniques are not very useful below 200 nm since oxygen is strongly absorbed at 200 nm and below. To study absorption below 200 nm, the instrument has to be evacuated—it is then termed as vacuum UV spectroscopy.

Spectrophotometers are of two types: single-beam and double-beam spectrophotometers.

Single beam spectrophotometer

A single-beam spectrophotometer consists of a single beam of light which passes through the sample (Fig. 17.7). Since there is only one light path, it is necessary to manually interchange the sample and reference solutions for each wavelength.

Double beam spectrophotometer

Double-beam instruments split the beam into two light beams of equal intensity. One beam passes through the reference solvent and the other passes through the sample solution (Fig. 17.8).

Double-beam instruments measure the absorbance of the solvent and solution simultaneously. The spectrophotometer electronically subtracts the absorption of the solvent in a reference beam from the absorption of the solution and measures the absorbance or transmittance characteristic of the compound alone. The intensity of absorbance versus the corresponding wavelength is recorded automatically on the graph. The spectrum is usually plotted as absorbance $A = \left(\log_{10} \frac{I_0}{I} \right)$ against wavelength λ (abscissa). The plot is often represented as ϵ_{\max} (extinction coefficient or molar absorptivity) against wavelength.

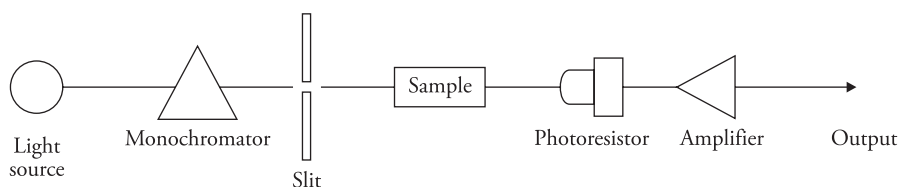


Figure 17.7 *Single-beam spectrophotometer*

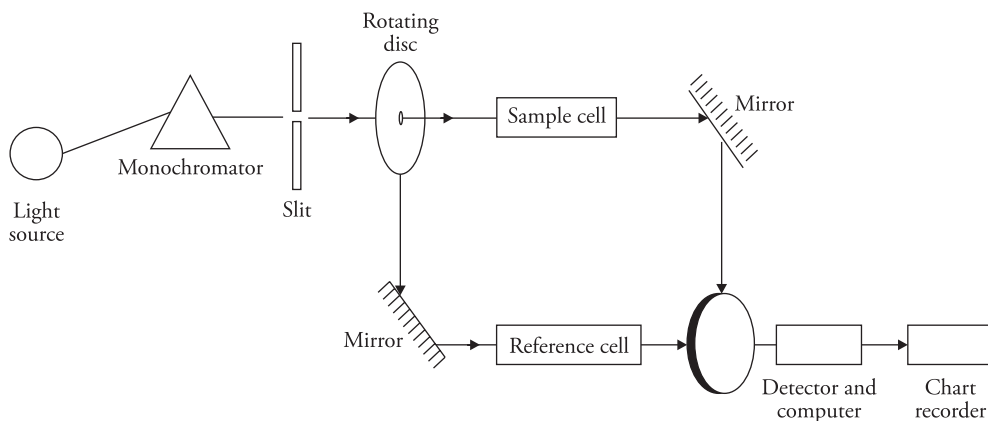


Figure 17.8 Double-beam spectrophotometer

Theory of electronic spectroscopy

When a molecule absorbs ultraviolet or visible light, its electrons are promoted from the ground state to a higher energy state. The electrons in the bonding molecular orbitals, for example, σ orbital, π orbital or non-bonding orbitals are promoted to anti-bonding molecular orbitals like σ^* and π^* (asterick * designates the anti-bonding orbital).

The following types of electronic transitions are possible.

$\sigma \rightarrow \sigma^*$ transitions The σ bonded electrons are held firmly in the molecule. Hence, the transitions from σ to σ^* require large amount of energy. These transitions **require high energy radiations and therefore, occur in the far ultraviolet region (~ 150 nm; high energy)**. Since oxygen of air absorbs strongly in this region, air has to be evacuated (vacuum ultraviolet spectroscopy). $\sigma \rightarrow \sigma^*$ transitions occur in **hydrocarbons like methane, propane and are less informative**.

$n \rightarrow \sigma^*$ transitions This type of transitions occur in saturated compounds with one hetero atom having unshared pairs of electrons (n electrons) like alcohols, ethers, amines, ketones, aldehydes, etc. The energy required for these transitions is lesser than the energy required for $\sigma \rightarrow \sigma^*$ transitions, for example, water absorbs at 167 nm, methyl alcohol at 174 nm and methyl chloride absorbs at 169 nm.

$\pi \rightarrow \pi^*$ transitions These transitions take place in compounds containing double and triple bonds. The excitation of π electrons requires lesser energy; hence they occur at longer wavelength. In unconjugated alkenes, absorption bands appear around 170–190 nm.

$n \rightarrow \pi^*$ transitions In these transitions, the electrons of the unshared electron pair on the hetero atom is excited to π^* anti-bonding orbital. As non-bonding electrons are loosely held, these require least energy and occur at larger wavelengths. They occur in unsaturated compounds with hetero atoms having unshared pairs of electrons like C = O, C = S.

Saturated aldehydes show both the transitions $n \rightarrow \pi^*$ transition occurring around 280 nm and $\pi \rightarrow \pi^*$ transition at around 180 nm. $n \rightarrow \pi^*$ transitions are less intense because the electrons in the n orbital are situated perpendicular to the plane of the π bond and hence the probability of electrons jumping from n to π^* is low.

The relative energies required for the various transitions follow the order.



The order is illustrated in Figure 17.9.

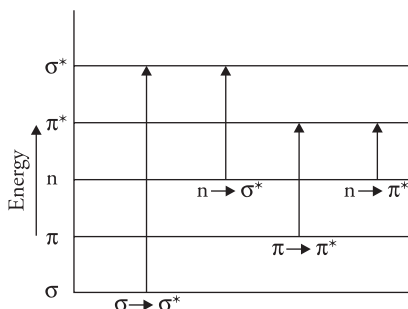


Figure 17.9 Energy of various electronic transitions

Transition probability

Depending upon the value of the extinction coefficient, transitions are classified as

- Allowed transitions
- Forbidden transitions

Allowed transitions are transitions with values of extinction coefficient ϵ_{\max} more than 10^4 . They generally arise due to $\pi \rightarrow \pi^*$ transitions.

The value of ϵ_{\max} for forbidden transitions is below 10^4 . Forbidden transitions are generally due to $n \rightarrow \pi^*$ transitions.

Benzophenone shows both types of transitions

- | | | | | |
|------|-------------------------|--------|-------------------|------------------|
| (i) | $\pi \rightarrow \pi^*$ | 252 nm | ϵ_{\max} | 20,000 (allowed) |
| (ii) | $n \rightarrow \pi^*$ | 325 nm | ϵ_{\max} | 180 (forbidden) |

Designation of bands

Absorption bands in UV spectroscopy may be designated by using electronic transitions such as ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc) or by using letters as described below.

- K-bands** They arise due to $\pi \rightarrow \pi^*$ transitions in conjugated π systems (from the German word *Konjugierte*). These bands are found in dienes, polyenes, enones, etc. They are allowed transitions and are intense ($\epsilon_{\max} > 10^4$).
- R-bands** They arise due to $n \rightarrow \pi^*$ transitions (from the German word *Radikal*). They have low molar absorptivities ($\epsilon_{\max} < 100$) and are forbidden transitions. They are observed in compounds with single chromophoric groups, that is, carbonyl or nitro.
- B-bands** These are benzenoid bands and are characteristic of aromatic and heteroaromatic compounds. They represent $\pi \rightarrow \pi^*$ transitions. In benzene, the B-band appears at 256 nm and displays fine structure, that is, the band contains multiple peaks.

- (iv) **E-bands** These are ethylenic bands and are also characteristic of aromatic systems like B-bands. The E_1 and E_2 bands of benzene occur near 180 nm and 200 nm, respectively, with ϵ value between 2000 and 1,4000.

Franck–Condon Principle

The Franck–Condon principle helps in interpreting the intensity distribution in an absorption spectrum. There is no selection rule and no quantum mechanical restrictions for vibrational quantum number v during an electronic transition, hence when a molecule undergoes electronic transition every transition from lower state represented by a double prime (v'') to higher state represented by a single prime (v') is possible. Hence many vibrational spectral lines are expected, all of which are not of the same intensity. The intensity of these spectra are explained by the Franck–Condon principle which states that *compared to the vibrational motion of the nuclei, the electronic transitions in a molecule take place so rapidly that the instantaneous internuclear distance is considered as unchanged during the electronic transition*. According to the Franck–Condon principle, the electronic transition is represented by a vertical line on a plot of potential energy versus the internuclear distance, and conventionally labelled according to the (v' , v'') numbers where the upper state is written first (0, 0), (1, 0), (2, 0) and so on. Generally all the molecules exist in the lowest vibrational state, that is, $v'' = 0$, hence all the transitions take place from the ground electronic state.

Figure 17.10 depicts the absorption transitions between the two electronic states in a diatomic molecule. Three situations arise, which are as follows:

1. The equilibrium internuclear distance between the lower and upper electronic states is equal. The most probable transition is $v'' = 0 \rightarrow v' = 0$ as it connects configurations of high probability and appears as a vertical line in accordance with the Franck–Condon principle. In this case ' r ' does not change during the electronic transition. This transition (0, 0) appears with maximum intensity. Transition to level $v' = 1, 2, 3, \dots$ (1, 0 and 2, 0) also occur but these involve a change in ' r ', thus deviating from the Franck–Condon principle and hence they lead to weak absorption bands.

Thus the absorption band (0, 0) appears with maximum intensity and the intensity decreases rapidly for higher bands (Fig. 17.10 a).

2. Figure 17.10 b shows the case when the internuclear distance in excited electronic state is slightly greater than the ground state. In this situation the most probable transition that satisfies the Franck Condon principle and connects to the configurations of maximum probability is $v'' = 0 \rightarrow v' = 2$. This band will be most intense and the bands corresponding to transitions to levels $v' = 0, 1, 3, 4, \dots$ will have lesser intensity (Figure 17.10 b).
3. Figure 17.10 c shows that the internuclear distance in upper electronic state is considerably greater than the lower electronic state. In such a case, a vertical electronic transition from the mid point of $v' = 0$ level is most likely to terminate in the continuum of the upper electronic state, thus dissociating the molecule. The spectrum is complex and is expected to consist of a progression of weak bands joined by a continuum of maximum absorption intensity.

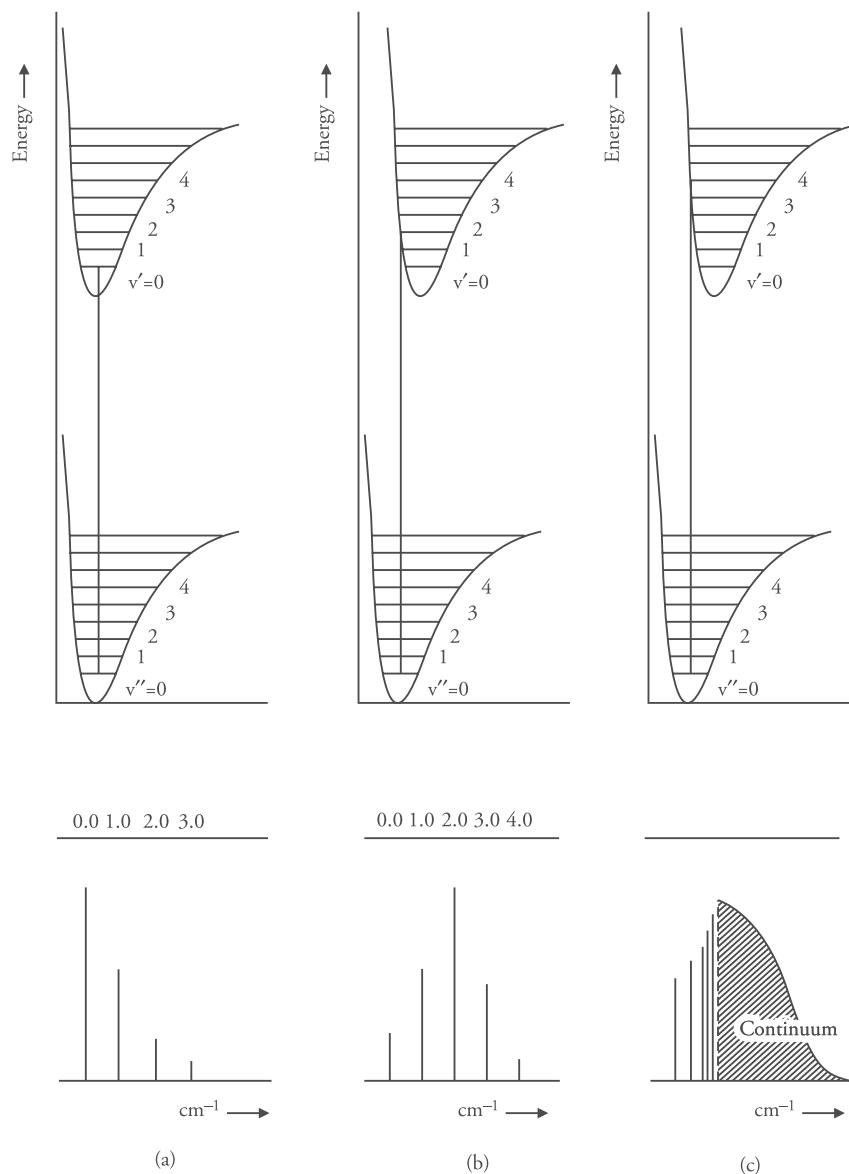


Figure 17.10 *Franck-Condon Principle (a) internuclear distances are equal in the upper and lower states, (b) internuclear distance in upper state is greater than in the lower state and (c) internuclear distance in the upper state is considerably larger.*

Chromophores and auxochromes

Chromophore Originally, a chromophore was considered as any system responsible for imparting colour to a compound.

For example, nitro compounds are generally yellow in colour. Hence, a nitro group is a chromophore which imparts yellow colour.

The term 'chromophore' has now been extended and redefined as *an isolated covalently bonded group that shows a characteristic absorption in the ultraviolet or the visible region*. Chromophores can be two types.

- (i) Those which contain π electrons and undergo $\pi \rightarrow \pi^*$ transitions. Example $C=C$, $-C\equiv C-$, etc.
- (ii) Those which contain both π electrons and non-bonding electrons. They undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Example : $>C=O$, $-C\equiv N$, $-N=N-$, etc.

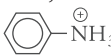
Auxochromes

An auxochrome is a colour enhancer. *It is defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength).*

It is a saturated group which when attached to a chromophore changes its intensity as well as wavelength of maximum absorption, for example OH, NH_2 and Cl. The effect of NH_2 on benzene is as follows.

Benzene absorbs at 255 nm with $\epsilon_{\max} = 203$, whereas aniline absorbs at 280 nm with $\epsilon_{\max} = 1430$. Hence amino group ($-NH_2$) is an auxochrome.

Absorption and intensity shifts

- (a) **Bathochromic shift (red shift)** A bathochromic shift is one in which the absorption maximum shifts towards a longer wavelength either due to the presence of an auxochrome or due to the effect of the solvent. Example $n \rightarrow \pi^*$ transitions of carbonyl compounds experience bathochromic shift when the polarity of the solvent is decreased.
- (b) **Hypsochromic shift (blue shift)** The shift of absorption maximum towards a shorter wavelength. It occurs due to the removal of conjugation or effect of solvent. For example, aniline absorbs at 280 nm because the pair of electrons on the nitrogen atom is in conjugation with the π bond system of the benzene ring. In acidic solutions, a blue shift is observed and absorption occurs at shorter wavelength (~203 nm). The  ion formed in acidic solutions does not have an electron pair and hence the conjugation is removed.
- (c) **Hyperchromic shift** Due to this effect, the intensity of absorption maximum increases, that is, ϵ_{\max} increases. It generally occurs due to the introduction of an auxochrome. For example, the B-bands of pyridine at 257 nm with $\epsilon_{\max} = 2750$ is shifted to 262 nm with $\epsilon_{\max} = 3560$ for methyl pyridine.
- (d) **Hypochromic shift** The intensity of absorption (ϵ_{\max}) maximum decreases due to this effect. Groups which distort the geometry of a molecule cause hypochromic shift. For example, biphenyl absorbs at 250 nm with $\epsilon_{\max} = 19,000$, whereas 2-methyl biphenyl absorbs at 237 nm with $\epsilon_{\max} = 10,250$. The introduction of the methyl group distorts the geometry of biphenyl.

The various shifts are shown in Figure 17.11.

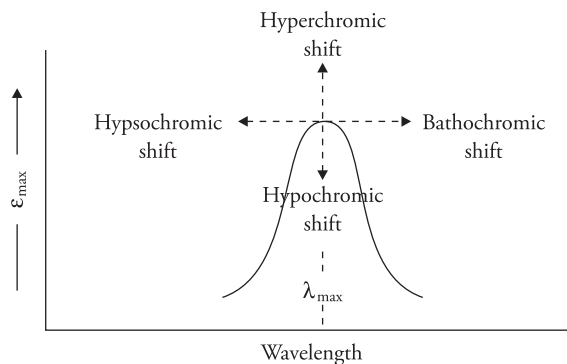


Figure 17.11 Absorption and intensity shifts

Solvent effects

The solvent used for preparing solutions should not absorb in the region under investigation. The most commonly used solvents in UV spectroscopy are ethanol, hexane, methanol, cyclohexane, etc.

The polarity of the solvent greatly affects the position and intensity of the absorption maximum.

The following shifts are observed on changing the solvent polarity.

- Non-polar compounds like ethylene, butadiene, aromatic hydrocarbons and conjugated hydrocarbons experience very little shift on changing the polarity of the solvent. The absorption maximum of non-polar compounds like ethylene is the same in alcohol (polar solvent) as well as in hexane (non-polar solvent).
- Polar compounds like α , β -unsaturated carbonyl compounds show two different shifts on changing the polarity of the solvent.

$n \rightarrow \pi^*$ transition (less intense) On increasing the polarity of the solvent, the $n \rightarrow \pi^*$ band moves to the shorter wavelength (blue shift). This is because the polar solvent stabilises n orbitals more than π^* orbitals. The energy of n orbital is thus lowered, increasing the energy gap between the ground state and the excited state. Hence, the absorption band moves to the shorter wavelength (Fig. 17.12). For example, absorption maximum of acetone is at 279 nm in hexane and 264 nm in water (polar solvent).

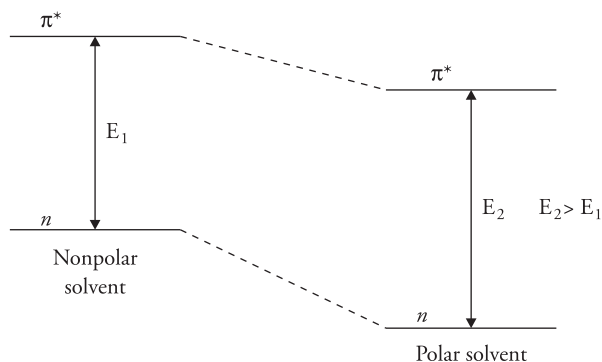


Figure 17.12 Absorption shift $n \rightarrow \pi^*$ band with change in solvent polarity

$\pi \rightarrow \pi^*$ transition (intense) On increasing the polarity of the solvent, the absorption band moves to the longer wavelength (red shift). This is because the dipole–dipole interactions with the solvent molecules lower the energy of the excited state more than that of the ground state (Fig. 17.13). In other words, hydrogen bonding with a polar solvent stabilises the π^* orbital because of greater polarity of π^* compared to π orbitals. Thus, the energy required for $\pi \rightarrow \pi^*$ transition is less and the absorption moves towards the red end of the spectrum (longer wavelength side). The value of the absorption maximum is greater in ethanol than that observed in hexane.

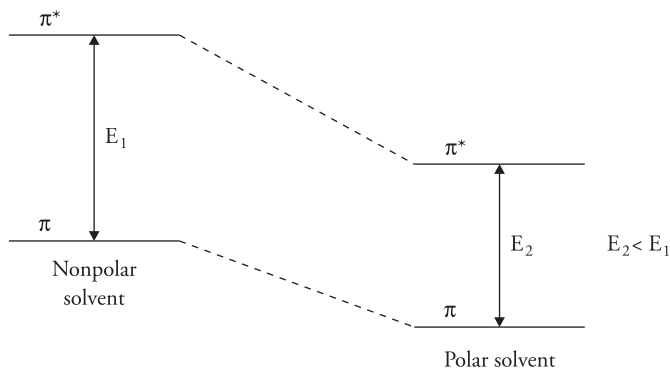


Figure 17.13 Absorption shift $\pi \rightarrow \pi^*$ transition with change in solvent polarity

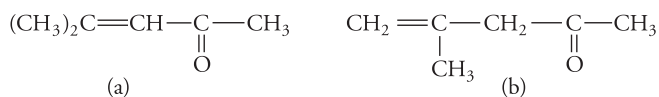
$n \rightarrow \sigma^*$ transitions in alcohols and amines experience blue shift (shift towards shorter wavelength) due to greater stabilisation of non-bonding electrons. Hence, the transition requires greater energy.

Applications of ultraviolet spectroscopy

Ultraviolet spectroscopy finds extensive use in the determination of structures of organic compounds. Some important applications of ultraviolet spectroscopy are as follows.

1. **Extent of conjugation** Conjugation lowers the energy required for $\pi \rightarrow \pi^*$ transition. The greater the extent of conjugation, the longer is the absorption wavelength. For example, ethylene absorbs at 170 nm due to $\pi \rightarrow \pi^*$ transitions whereas butadiene having two double bonds absorbs at 217 nm, and a polyene with eight conjugated double bonds absorbs at about 420 nm, that is, in the visible region and they appear coloured to the human eye. Similarly, lycopene with eleven conjugated double bonds absorbs at 454 nm and imparts red colour to tomatoes.
2. **Determination of geometrical isomers** Effective $\pi \rightarrow \pi^*$ transitions take place when the molecule is coplanar. The steric strain in *cis*-isomer prevents coplanarity. Thus, *cis* isomers absorb at a shorter wavelength when compared to the *trans*-isomer, for example, *cis*-stilbene absorbs at 280 nm and *trans*-stilbene absorbs at 295 nm.
3. **Identification of unknown compounds** Unknown compounds can be identified by comparing its spectra with the spectra of known compounds. Identical spectra reveal identical structure and if the spectra is different, then the structure is different.

4. **Distinction between conjugated and non-conjugated compounds** Consider the following compounds.



Compound (a) has longer λ_{max} values because C = O group is in conjugation with the double bond.

5. **Detection of impurities** Ethanol contains benzene as an impurity. Since benzene is toxic in nature, it is essential to detect its presence. The presence of benzene can be detected through the UV spectrum of the sample at 280 nm (Fig. 17.14). Ethanol is transparent at this wavelength but benzene shows an absorption band with $\epsilon_{\text{max}} = 230$.
6. **Detection of hydrogen bonding** Hydrogen bonding can be detected on the basis of the shift absorbed in polar solvents.
7. **Quantitative analysis** This is based on Beer–Lambert’s law

$$A = \epsilon c l$$

where A = absorbance at a particular wavelength

c = concentration of the sample

ϵ = constant termed as molar absorptivity or extinction coefficient.

The absorbance of the standard solution (A_1) and the unknown solution (A_2) are measured in a sample cell. If the concentration (c_1) of the standard solution is known, the concentration (c_2) of the sample can be determined as follows

$$\frac{A_1}{A_2} = \frac{c_1}{c_2}$$

Example For a solution of camphor in hexane in a 5-cm cell, the absorbance A was found to be 2.52 at 295 nm with $\epsilon_{\text{max}} = 14$. What is the concentration of camphor?

Solution

$$A = \epsilon c l$$

$$A = 2.52 \quad c = ? \quad \epsilon = 14 \quad l = 5 \text{ cm}$$

$$\therefore 2.52 = 14 \times c \times 5$$

$$c = \frac{2.52}{14 \times 5} = 3.6 \times 10^{-2} \text{ mol/L}$$

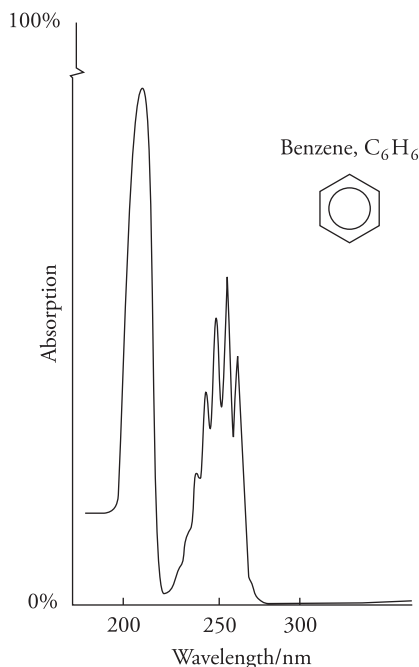


Figure 17.14 *UV absorption spectra of benzene in ethanol*

17.4 IR Spectroscopy

Introduction

Infrared spectroscopy is a very important tool for the determination of the structure of a compound. It is also called vibrational spectroscopy as it involves the transition between vibrational energy levels. Infrared radiations do not have sufficient energy to bring about electronic excitation; however, it causes atoms and groups to vibrate about the covalent bond connecting them. As these vibrations are quantised, the compound absorbs the infrared energy in different regions of the spectrum. An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared radiation absorbed. Apart from vibrational changes, rotational changes also occur in the molecule, hence some fine structures are obtained on the vibrational band.

The IR region of electromagnetic spectrum extends from $0.8\ \mu$ to $200\ \mu$ ($12,500\ \text{cm}^{-1}$ to $50\ \text{cm}^{-1}$) but the most important region for the purpose of study is $2.5\ \mu$ to $15\ \mu$ ($4000\ \text{cm}^{-1}$ to $667\ \text{cm}^{-1}$). Molecular vibrations are detected and measured in this region. The region from $0.8\ \mu$ to $2.5\ \mu$ is called near infrared and that from $15\ \mu$ to $200\ \mu$ is called far infrared region.

Infrared spectrum

When a beam of IR radiation of varying frequency passes through a sample, it absorbs energy when the energy matches the difference between the vibrational energy levels of its bonds. Absorption

bands are thus obtained. Infrared spectrum is usually plotted with the percentage transmittance rather than the absorbance as ordinate. This makes the absorption bands appear as dips or troughs rather than as maxima as in the case of ultraviolet and visible spectra. These dips or troughs are called bands and they represent absorption of infrared radiation at that frequency of the sample. The bands can be strong, medium or weak depending upon the absorption.

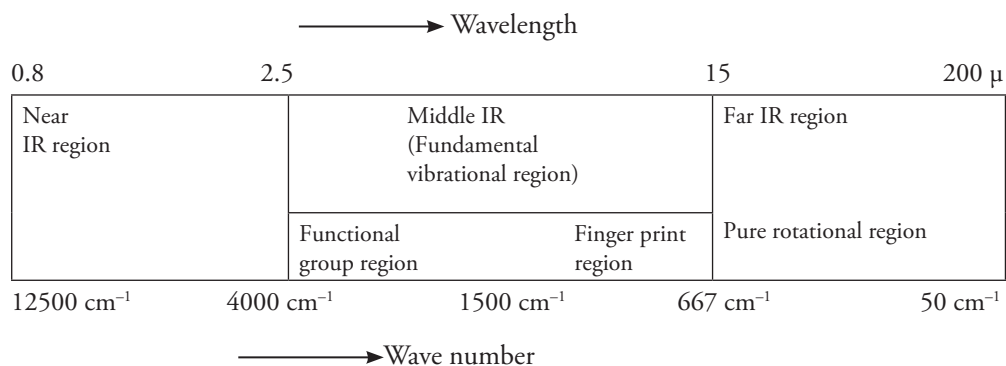
The position of the infrared absorption band is specified in frequency units expressed not in hertz but in wave numbers, cm^{-1} or by its wavelength λ measured in micrometers (μm).

$$\bar{\nu} = \frac{1}{\lambda(\text{in cm})} \quad \text{or} \quad \bar{\nu} = \frac{10,000}{\lambda(\text{in } \mu\text{m})}$$

Band intensity is expressed either in terms of absorbance (A) or transmittance (T)

$$A = \log_{10} (1/T)$$

IR spectroscopy is divided into three regions:



- The near IR region extends from 12500 cm^{-1} to 4000 cm^{-1} wave number. It is of little significance as there are few absorptions in this range.
- The most important and useful region extends from 4000 cm^{-1} to 667 cm^{-1} . Most absorptions occur in this region.
- The far infrared region deals with the pure rotational motion of the molecule. Very few absorptions appear in this region. It extends from 667 cm^{-1} to 50 cm^{-1} .

Instrumentation

The instrument consists of the following.

- Light source** Infrared radiations are produced by electrically heating Globar or a Nernst filament to 1000–1800 °C. Globar is a rod of silicon carbide, whereas the Nernst filament is a high resistance element composed of sintered oxides of zirconium, cerium and thorium.
- Filter or monochromator** Optical prisms or gratings are used to obtain monochromatic light. Glass or quartz cannot be used as the prism material because they absorb in the infrared region. Prisms are made of sodium chloride or alkali metal halides.

- (iii) **Sample holder** Cells are made of NaCl or alkali metal halides as they do not absorb IR radiations. Solid samples are ground with KBr and made into a disc. The sample should be absolutely dry as water absorbs strongly in the IR region. Solvents used for IR are chloroform, carbon tetrachloride, carbon disulphide, etc.
- (iv) **Detectors** Thermocouple based detectors are used. Light from the source is split into beams, one of which passes through the sample and the other through the reference. The beam on passing through the sample becomes less intense. There is a difference in intensity of the two beams. This is detected and recorded and an IR spectrum is obtained.

The schematic diagram of an IR spectrophotometer is shown in Figure 17.15.

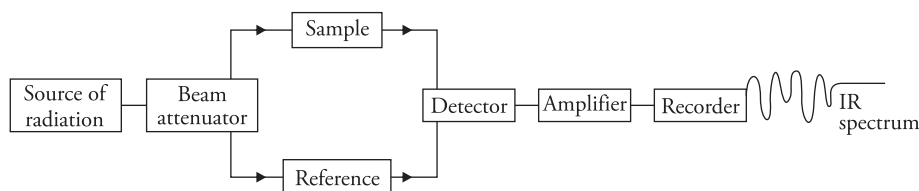


Figure 17.15 Schematic diagram of IR spectrophotometer

Theory: Absorption of infrared radiation and molecular vibrations

Covalent bonds behave like tiny springs connecting the atoms. The atoms in the molecules do not remain in a fixed position but vibrate. This vibrational motion is quantised. At room temperature, the molecules of a sample are in their lowest vibrational state. When infrared radiation is passed through the sample, the molecule absorbs radiation of appropriate energy and gets excited to a higher vibrational level (Fig. 17.16). It is important to note here that IR light is absorbed only when the dipole moment of the molecule is different in the two vibrational levels and the oscillating dipole moment due to molecular vibrations interacts with the oscillating electric vector of the infrared beam.

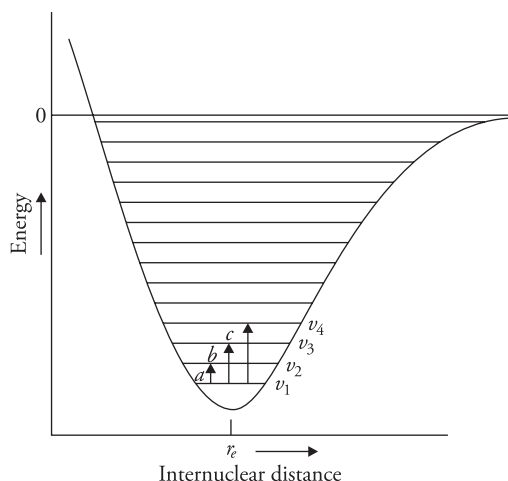


Figure 17.16 Vibrational spectra of diatomic molecules

Types of vibrations

There are two types of vibrations.

- (a) **Stretching** In this type of vibrations, the distance between the atoms increases or decreases but the atoms remain in the same bond axis. Stretching can be of two types:
- (i) Symmetric
 - (ii) Asymmetric
- (i) **Symmetric stretching** In symmetric stretching, the movement of the atoms with respect to a particular atom is in the same direction (Fig. 17.17).

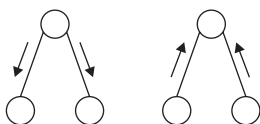


Figure 17.17 Symmetric stretching

- (ii) **Asymmetric stretching** In these vibrations, one atom approaches the central atom and the other departs from it (Fig. 17.18).

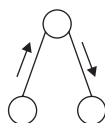


Figure 17.18 Asymmetric stretching

- (b) **Bending vibrations** In these types of vibrations, the position of the atom changes with respect to the original bond axis but the distance between the atoms remains constant. Bending vibrations are of two types.

- (i) **In-plane bending vibrations** In this type, the atoms remain in the same plane as the nodal plane of the system. These, also, are of two types.

Scissoring In this type, the two atoms approach each other and move away like the two arms of a scissors (Fig. 17.19 a).

Rocking In this type, both the atoms move in the same direction (Fig. 17.19 b).

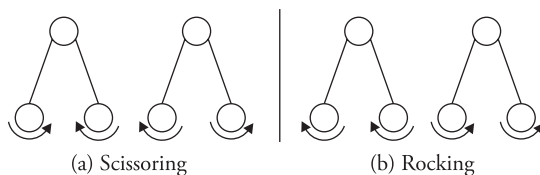


Figure 17.19 In-plane bending vibrations

- (ii) **Out-of-plane bending vibrations** The atoms move out of the nodal plane with respect to the central atom. These are again of two types.

Wagging In this type, both the atoms swing up and down with respect to the central atom (Fig. 17.20).

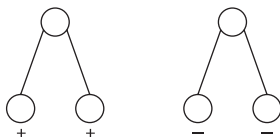


Figure 17.20 Out-of-plane bending-wagging

Twisting In this type, one atom moves up the plane and the other moves down the plane with respect to the central atom (Fig. 17.21).

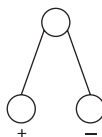


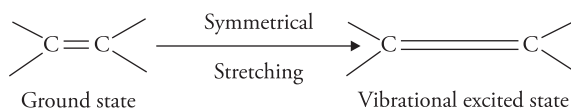
Figure 17.21 Out-of-plane bending-twisting (the signs + and – indicate movement towards and away from the reader)

Remember that it takes more energy to stretch a spring than to bend it; hence, stretching vibrations appear at a higher frequency as compared to the bending vibrations.

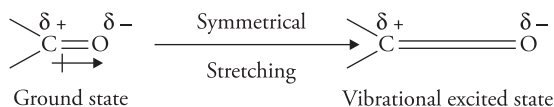
Dipole moment and infrared spectrum

All types of molecules cannot interact with IR radiation. Only those molecules which undergo a net change in dipole moment because of its vibrational or rotational motion absorb in the IR region. Homonuclear diatomic molecules like H_2 , O_2 , N_2 or Cl_2 do not show change in dipole moment during vibration and hence they do not absorb in the infrared region. Such molecules are termed as *infrared inactive*.

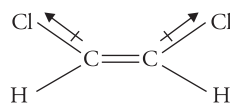
As stated earlier, infrared radiation is absorbed when the oscillating dipole moment interacts with the oscillating electric vector of the infrared beam. For such an interaction to occur, the dipole moment of the molecule in the ground state and the vibrational excited state should be different. The greater the difference in these dipole moments, the more intense is the absorption. For example, the symmetrical stretching vibration of the C–C bond in ethylene can be represented as



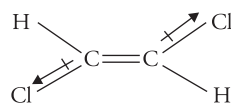
Symmetrical stretching of a carbonyl group can be expressed as



$\text{C}=\text{C}$ is non-polar, hence, on symmetrical stretching, there is little or no change in dipole moment and hence, the infrared absorption is either absent or very weak. However, the carbonyl group ($\text{C}=\text{O}$) is polar due to the different electronegativities of the atoms. On stretching, the dipole moment increases considerably. This change in dipole moment leads to the generation of an oscillating electric field. If the frequency of this oscillating electric field is equal to the frequency of the fluctuating electric field of the infrared radiation, the energy is absorbed or emitted resulting in an infrared spectrum. Hence ($\text{C}=\text{O}$) is *infrared active* and will show an intense absorption. Similarly, the trans-isomer is non-polar having zero dipole moment. On stretching, the



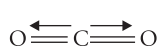
Dipole moment
 $\mu = 2.95 \text{ D}$
cis - 1, 2 dichloroethene



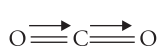
$\mu = 0$
trans - 1, 2 dichloroethene

dipole moment does not change; hence, it is infrared inactive. On the other hand, the cis-isomer undergoes change in dipole moment and hence, it is infrared active.

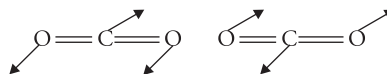
Some molecules do not have a permanent dipole moment but some of their vibrational modes are accompanied by change in dipole moment making them infrared active. For example, the symmetrical stretching of $\text{C}=\text{O}$ in CO_2 is infrared inactive while asymmetrical stretching and bending vibrations are infrared active.



(a) Symmetrical stretching
(IR inactive)



(b) Asymmetrical stretching
(IR active)



(c) Bending vibrations
(IR active)

Vibrational Spectra

Simple harmonic oscillator model: Consider a diatomic molecule associated with a dipole moment. The vibrational motion of atoms of a diatomic molecule may be similar to the vibration of a simple harmonic oscillator. In such an oscillator the force required to restore an atom to its original state is proportional to the displacement of the vibratory atom from its original position in accordance with the Hooke's law. If Δx is the displacement in the vibratory atom from its original position then according to Hooke's law, restoring force

$$F \propto \Delta x$$

$$F = -kx \quad (1)$$

k is the force constant (units of k are N m^{-1} , that is, force per unit distance), $x = r - r_e$, where r is the distance to which the atoms have been stretched and r_e is the equilibrium distance between the two atoms. The potential energy of a simple harmonic oscillator as a function of displacement from equilibrium configuration is given by the Hooke's law equation

$$V_{(x)} = \frac{1}{2} kx^2 \quad (2)$$

This is the equation for a parabola. Hence a parabolic potential energy curve is obtained

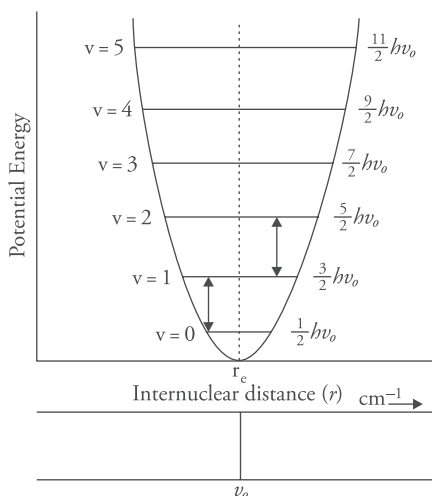


Figure 17.22 Potential energy diagram for a harmonic oscillator

The vibrational frequency of a point mass m connected by a spring of force constant k is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (3)$$

where μ is the reduced mass. If m_1 and m_2 are the masses of the two atoms then

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The solution of Schrodinger wave equation for a simple harmonic oscillator gives quantised vibrational energy levels

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad (E_v \text{ in joules}) \dots (4)$$

v is the vibrational quantum number with the allowed values 0, 1, 2, 3 and ν is the frequency of vibration given by Eq. (3). On solving equation 4 for $v = 0, 1, 2, 3$, the values of E_v work out to be $\frac{1}{2}h\nu$, $\frac{3}{2}h\nu$, $\frac{5}{2}h\nu$, $\frac{7}{2}h\nu$, respectively, which shows that the quantised energy levels are equally spaced as shown in Figure 17.22. It is also clear that the lowest energy level at $v = 0$ is not zero but E_v for $v = 0$ is $\frac{1}{2}h\nu$ and this is termed as the *zero point energy* of the molecule.

Vibrational Spectrum for Simple Harmonic Oscillator

Energy levels of harmonic oscillator: If a diatomic molecule undergoes transitions from upper vibrational level $v+1$ to lower vibrational level v , the change in vibrational frequency is given by

$$\Delta E_v = \left[\left(v + 1 \right) + \frac{1}{2} \right] h\nu - \left(v + \frac{1}{2} \right) h\nu$$

$$\Delta E_v = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

where $\bar{\nu}$ is the wave number

Thus for a diatomic molecule two consecutive energy levels are equally spaced and they are equal to $hc\bar{\nu}$.

Selection rule

The selection rule for vibration transition in a simple harmonic oscillator is

$$\Delta v = \pm 1 \quad (6)$$

The positive sign indicates absorption spectra and the negative sign indicates emission spectra. Hence transition from any v to $v + 1$ level will give the same energy change and hence only one line is expected. Moreover at room temperature most of the molecules are in ground vibrational state ($v = 0$) hence the transitions will occur only from $v = 0$ to $v = 1$ and the vibrational frequency corresponding to this is the *fundamental vibrational frequency*.

Anharmonic Vibrations

In a harmonic oscillator model the restoring force is proportional to displacement and the energy of harmonic oscillator is given by

$$E_v = \left(v + \frac{1}{2} \right) hc\bar{\nu} \quad (7)$$

where v is the vibrational quantum number. In harmonic oscillator model the diatomic molecule reaches equilibrium state and it can never dissociate, but for a real molecule this is not true. The movement of a real oscillator is not perfectly harmonic because as displacement increases the

restoring force becomes weaker and for large amplitude of vibration, the atoms must fall apart, that is, the molecule must dissociate into atoms. Such a real oscillator is said to be an *anharmonic oscillator*. P.M. Morse in 1929 suggested an empirical expression for the potential energy of an anharmonic diatomic oscillator, given by

$$V(r) = D_e \left[1 - e^{\alpha(r-r_e)} \right]^2 \quad (8)$$

where α is a constant, D_e is the dissociation energy of the molecule. If $V(r)$ is plotted as a function of r we obtain a sketch, as shown in Figure 17.23.

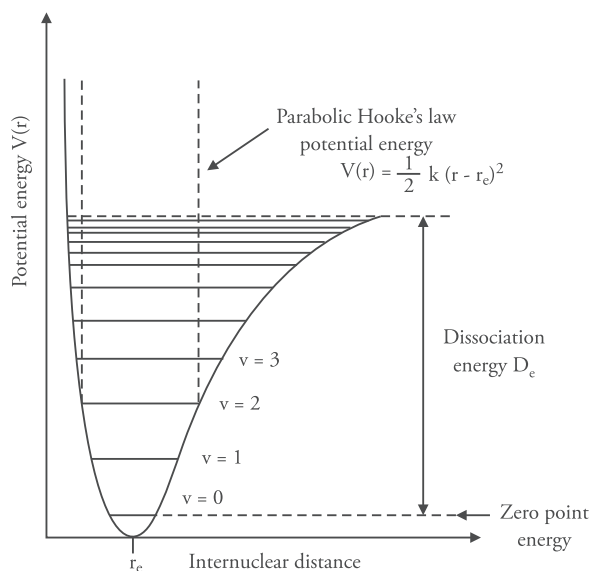


Figure 17.23 Morse potential energy for an anharmonic diatomic oscillator

On solving the Schrodinger wave equation for an anharmonic oscillator using the Morse potential energy, the energy levels are given by

$$E_v = \left(v + \frac{1}{2} \right) h \bar{\nu}_e - \left(v + \frac{1}{2} \right)^2 h x_e \bar{\nu}_e \quad (E_v \text{ in joules}) \quad (9)$$

where $\bar{\nu}_e$ is the equilibrium oscillation frequency and x_e is the anharmonicity constant (a small positive number) and $v = 0, 1, 2, 3 \dots$

As expected $v x_e \ll \bar{\nu}_e$; the consequence of this is that the vibrational energy levels of SHO are slightly lowered and the successive energy levels are not equally spaced, they come closer and closer as the quantum number increases (remember in harmonic oscillator model the energy levels were equally spaced). Moreover for anharmonicity the selection rule is no longer $\Delta v = \pm 1$ but transitions corresponding to $\Delta v = \pm 2, \pm 3, \dots$ are also observed. Hence the selection rule for anharmonic oscillator is

$\Delta v = \pm 1, \pm 2, \pm 3$ and so on.

Transitions from $v = 0$ to $v = 1$ is most intense as the ground energy level is populated and is called the fundamental absorption or fundamental band. The transition from $v = 0$ to $v = 2$ has a weak intensity and is the first overtone; $v = 0$ to $v = 3$ is the second overtone with still lesser intensity.

Solved Examples

(i) Of the following, which one is expected to absorb at higher frequency for stretching vibration?

- (a) $C \equiv C$ and $C = C$ (b) $C-H$ and $C-C$
 (c) $O-H$ and $C-C$ (b) $C = C$ and $C-C$

Ans (a) $C \equiv C$ (b) $C-H$ (c) $O-H$ (d) $C = C$

Solution This is because the bond strength of $C \equiv C$, $C-H$, $O-H$ and $C = C$ are greater than that of $C = C$, $C-C$, $C-C$ and $C-C$, respectively.

(ii) Calculate the vibrational absorption frequency of the carbonyl, $>C=O$ group, if the force constant for the double bond is 1×10^6 dynes cm^{-1}

Solution

$$\text{Mass of oxygen atom} = \frac{16}{6.023 \times 10^{23}} \approx 2.65 \times 10^{-23} \text{ g (approx)}$$

$$\text{Mass of carbon atom} = \frac{12}{6.023 \times 10^{23}} \approx 2.00 \times 10^{-23} \text{ g (approx)}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} = \frac{1}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{1 \times 10^6}{\frac{2.65 \times 10^{-23} \times 2.00 \times 10^{-23}}{2.65 \times 10^{-23} + 2.00 \times 10^{-23}}}} = 1581 \text{ cm}^{-1}$$

Practice problems

1. Calculate the approximate frequency of the $C-H$ stretching vibration from the following data.

$$k = 5 \times 10^5 \text{ g s}^{-2}$$

$$\text{Mass of carbon atom } (m_1) = 20 \times 10^{-24} \text{ g}$$

$$\text{Mass of hydrogen atom } (m_2) = 1.6 \times 10^{-24} \text{ g}$$

[Ans 3100 cm^{-1}]

2. Calculate the approximate wavelength of absorption associated with the C–H bond in the stretching vibration of the methyl group. The force constant for the single bond is 5×10^5 dynes cm^{-1} . The masses of carbon and hydrogen are 20×10^{-24} g and 1.6×10^{-24} g, respectively.

$$[\text{Ans } \bar{\nu} = 3023 \text{ cm}^{-1} \quad \lambda = 3.31 \times 10^{-4} \text{ cm} = 3.31 \text{ } \mu\text{m}]$$

Number of fundamental vibrations for polyatomic molecules Polyatomic molecules show more than one fundamental band. The number of fundamental bands of a polyatomic molecule depends upon the degrees of freedom in a molecule. The number of degrees of freedom is equal to the sum of the coordinates necessary to locate all the position of the atoms in space. The position of an atom is specified by the three cartesian coordinates (x , y , z). Hence, its degree of freedom is three. The degree of freedom of an atom and molecule are given in Table 17.3.

Table 17.3 Degrees of freedom

	Types of degree of freedom	Total degree of freedom
Isolated atom	Only translational degree of freedom (it does not have rotational and vibrational degree of freedom)	3
Molecule	Translational + rotational + vibrational degree of freedom	$3n$ where n is the number of atoms in a molecule

We are concerned only with the vibrational degree of freedom which gives the number of fundamental bands. Therefore, let us calculate the vibrational degree of freedom for different types of molecules.

(a) **For linear molecules of n atoms**

$$\text{Total degrees of freedom} = 3n$$

$$\text{Translational degree of freedom} = 3$$

$$\text{Rotational degree of freedom} = 2$$

$$\therefore \text{Vibrational degree of freedom} = 3n - 3 - 2 = 3n - 5$$

$$\therefore \text{Number of fundamental bands for a linear molecule} = 3n - 5.$$

Rotation about the axis of linearity does not bring about any change in the position of atoms while rotation about the other two axes, changes the position of the atoms. Hence, linear molecule has two degrees of rotation.

(b) **For non-linear molecules of n atoms**

$$\text{Total degrees of freedom} = 3n$$

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = $3n - 3 - 3 = 3n - 6$

Hence, number of fundamental bands = $3n - 6$

Combination bands and Fermi resonance

Combination bands, difference bands or overtones are produced due to the interaction of the vibrational states in polyatomic molecules. If there are two fundamental bands at a and b , then the additional bands that can be expected are

- (i) $2a, 2b$ (overtones)
- (ii) $a + b, a + 2b, 2a + b$, etc. (combination bands)
- (iii) $a - b, a - 2b, 2a - b$, etc. (difference bands)

The intensity of these bands is 10–100 times less than the intensity of the fundamental bands. When an overtone or combination band falls near the fundamental band, there is resonance and the molecule transfers its energy from the fundamental to the overtone band and back. Due to this resonance, both the bands share their intensity and appear as a pair of equally intense bands in the IR spectrum. Such type of resonance is known as *fermi resonance*.

Solved Examples

- (i) Calculate the theoretical number of vibrational degrees of freedom in
 - (a) Carbon dioxide
 - (b) Benzene
 - (c) Water
 - (d) Sulphur dioxide
 - (e) N_2O

Solution

- (a) CO_2 is a linear triatomic molecule

Vibrational degree of freedom = $3n - 5$ where $n = 3$

$$= 3 \times 3 - 5 = 4$$

- (b) C_6H_6 is a non-linear molecule where $n = 12$ ($6C + 6H$)

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 12 - 6 = 30$$

30 fundamental bands are expected in benzene but the number is less as the bands may fall outside the region under investigation or may be too weak to be observed as bands.

- (c) H_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3 \times 3 - 6 = 3$

- (d)
- SO_2
- is a non-linear molecule with
- $n = 3$

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 3 - 6 = 3$$

- (e)
- N_2O
- is a non-linear molecule with
- $n = 3$

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 3 - 6 = 3$$

Practice Problems

- (i) Calculate the theoretical number of vibrational degrees of freedom in

(a) HCN

(b) $\text{C}_6\text{H}_5\text{CH}_3$ (c) CH_4

[Ans (a) 4 (b) 39 (c) 9]

Factors influencing vibrational frequencies

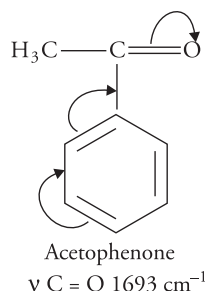
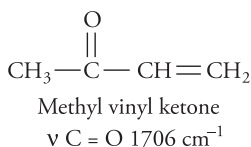
The vibrational frequency as calculated by Hook's law and that obtained experimentally usually differs due to various factors which influence the vibrational frequencies. The factors are explained below.

- Physical state** A compound absorbs at a higher frequency in vapour state than when it is in solid or liquid state. For example, cyclopentanone shows carbonyl absorption in the vapour phase at 1772 cm^{-1} and in the liquid phase at 1746 cm^{-1} . Carbonyl stretching frequency of acetone in vapour phase is 1742 cm^{-1} and in liquid phase, it lowers to 1718 cm^{-1} .
- Electronic effects** Inductive effects, mesomeric effects change the force constant or bond strength and affect vibrational frequency. Some examples are given below.

Compound	HCHO	CH_3CHO	CH_3COCH_3
Absorption (cm^{-1})	1750	1745	1715

Introduction of alkyl group (+ I effect) causes lengthening or weakening of the bond, hence the force constant is lowered and the wave number of absorption decreases.

Similarly,



In the above case, the mesomeric effect dominates over the $-I$ effects of $-\text{CH}=\text{CH}_2$ and C_6H_5- group. Thus, the absorption frequency of $-\text{C}=\text{O}$ group falls.

3. **Hydrogen bonding** Hydrogen bonding brings about downward frequency shifts. The stronger the hydrogen bonding, the greater is the absorption shift towards the lower wave number. Infrared spectroscopy helps in differentiating between inter- and intramolecular hydrogen bonding. Intermolecular hydrogen bonding gives rise to broad absorption bands which are concentration-dependent. Bands arising from intramolecular hydrogen bonding are sharp and independent of concentration. For example, in aliphatic alcohols, a sharp band appears at 3650 cm^{-1} in dilute solutions due to free $\text{O}-\text{H}$ group while a broad band appears at 3350 cm^{-1} due to hydrogen bonded OH group.
4. **Effect of solvent** Change in solvent shifts the IR band. For example, the carbonyl stretching frequency of acetone is different in different solvents.

Solvent	Hexane	Chloroform	Ethanol
Absorption band	1726 cm^{-1}	1713 cm^{-1}	1709 cm^{-1}

5. Coupled vibrations and Fermi resonance

Vibrational frequency changes due to interaction between fundamental vibration and overtones (Fermi resonance). For example, in aldehydes $\text{C}-\text{H}$ stretching absorption usually appears as a doublet ($\sim 2820\text{ cm}^{-1}$ and 2720 cm^{-1}) due to interaction between $\text{C}-\text{H}$ stretching (fundamental band) and the overtone of $\text{C}-\text{H}$ deformation (bending vibration).

Applications of infrared spectroscopy

Infrared spectroscopy is a very important tool used to determine the structures of organic compounds. A great advantage of IR spectroscopy is that it can study virtually any sample state from liquids to solutions, pastes, powders, films, fibres, and so on; all can be examined by the judicious use of sampling techniques.

Table 17.4 gives the characteristic IR absorption frequencies of important functional groups that help in their identification

Infrared spectrum is usually studied under two regions

- (a) Functional group region ($4000 - 1500\text{ cm}^{-1}$)
- (b) The finger print region ($1500 - 667\text{ cm}^{-1}$)

The higher frequency region $4000 - 1500\text{ cm}^{-1}$ is called the functional group region. The characteristic stretching frequencies of all the important functional groups such as OH , NH_2 , $\text{C}=\text{O}$, etc., lie in this region. The region below 1500 cm^{-1} ($1500-667\text{ cm}^{-1}$) is rich in absorptions caused by bending vibrations and those resulting from the stretching vibrations of $\text{C}-\text{C}$, $\text{C}-\text{O}$ and $\text{C}-\text{N}$ bonds. These bands are unique to an organic compound just like finger prints are characteristic to an individual. Hence, this region is termed as the fingerprint region.

Table 17.4 Characteristic IR absorption frequencies of important functional groups that help in their identification

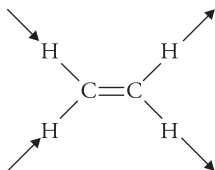
Group	Type of vibration	Region (in cm^{-1}) and intensity
alkane	C-H str C-C str C-H def	2960-2850(m, s) 1300-800(w) 1485-1440(m)
alkenes	$>\text{C}=\text{C}-\text{H}$ str C=C str	3100-3000 (m) 3090-3075 (m) ~ 1675 (m)
non conjugate diene	C=C str	1650-1600 (v) variable
conjugate diene	C=C str	~1600 (w) ~ 1650 (w)
alkynes	$\text{C}\equiv\text{C}-\text{H}$ str C-H def	3300 (s) 650-610 (s)
aromatic	Ar-H str C=C str C-H def	3050-3000 (v) variable 1600 (v) 1580 (v) 1500 (m) 1450 (m) 900-700 (m)
mono substituted	C-H def	710-690 (s) 770-730 (s)
Disubstituted (meta)	C-H def	710-690 (m) 800-750 (m)
Disubstituted (ortho)	C-C def	770-735 (v, s)
Disubstituted (para)	C-H def	840-800 (m)
Alcohols Free O-H group	O-H str	3700-3500 (v, sh)
Intermolecular hydrogen bonded OH	O-H str	3400-3200 (v, b)
Intramolecular hydrogen bonded OH	O-H str	3570-3450 (v)
Primary alcohols	C-O str	1350-1260 (s) 1050 (s)
Secondary alcohols	C-O str	1350-1260 (s) 1100 (s)
Tertiary alcohols	C-O str	1400-1310 (s) 1150 (s)

Phenols	C-O str	~ 1200 (s) 1410-1300 (s)
Saturated aldehydes	C=O str	1740-1720 (s)
HCHO	C=O str	1750 (s)
CH ₃ CHO	C=O str	1745 (s)
Carboxylic acids	O-H str (bonded)	3000-2500 (w, b)
Saturated aliphatic acids	C=O str	1725-1700 (s)
Primary amides	C=O str N-H str N-H str (hydrogen bonded) N-H (def)	~ 1690 (s) ~ 3500 (m) ~ 3400 (m) ~ 3350 (m) ~ 3180 (m) 1620-1590 (s)
Saturated esters	C=O str	1750-1735 (s)
α, β - unsaturated ester	C=O str	1730-1715 (s)
Primary amines	N-H str (sym and asym)	3500-3300 (m) (two sharp bands)
secondary	N-H str	3500-3300 (m) (one band)

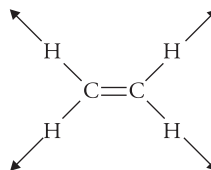
Solved Problems

1. Indicate whether the following vibrations will be IR active or inactive

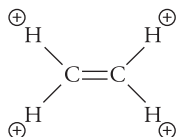
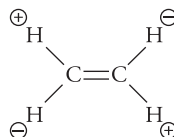
Molecule	Motion
(a) CH ₃ —CH ₃	C—C stretching
(b) CH ₃ —CCl ₃	C—C stretching
(c) SO ₂	Symmetric stretching
(d) CH ₂ =CH ₂	C—H str (shown on next page)
(e) CH ₂ =CH ₂	C—H str (shown on next page)
(f) CH ₂ =CH ₂	CH ₂ wagging (shown on next page)
(g) CH ₂ =CH ₂	CH ₂ twisting (shown on next page)



(d) C—H str



(e) C—H str

(f) CH₂ wagging(g) CH₂ twisting

Answer (a) Inactive (b) Active (c) Active (d) Active
 (e) Inactive (f) Active (g) Inactive

2. The following characteristic peaks were observed in the infrared spectrum of an organic compound having the formula C₂H₆O.

- (a) Strong band at 3300 cm⁻¹ (b) Band at 2965 cm⁻¹
 (c) Band at 2920 cm⁻¹ (b) Band at 1050 cm⁻¹

Name the compound.

Solution

- Peak at 3300 cm⁻¹ indicates the presence of —OH group.
- Strong band at 1050 cm⁻¹ confirms the presence of primary alcoholic group.
- Band at 2965 and 2920 cm⁻¹ may be due to C—H stretching.

Hence the compound contains a primary alcoholic group. As the molecular formula is C₂H₆O, the structure of the given compound is CH₃CH₂OH (ethyl alcohol).

3. Give the characteristic absorption peaks of CH₃COOH.

Solution

- CH₃COOH spectrum will have the following characteristic peaks.
 - Broad band at 3030–3040 cm⁻¹ due to hydrogen bonded O—H stretching of carboxylic acid.
 - Band at 1720 cm⁻¹ due to carbonyl (C=O) stretching of a saturated chain carboxylic acid.
 - A band at 1280 cm⁻¹ due to C—O stretching of —COOH group.
 - A band at about 940 cm⁻¹ due to O—H bending of —COOH group.
4. Give the characteristic absorption bands in the infrared spectrum of benzaldehyde.

Solution

- A band at 3080 cm^{-1} due to C–H stretching of benzene ring.
 - Bands at 2680 cm^{-1} and 2780 cm^{-1} due to C–H str. of an aldehyde group
 - A band at 1700 cm^{-1} due to C=O str. of an aromatic benzene ring.
 - Bands at 745 cm^{-1} and 685 cm^{-1} due to C–H bending of monosubstituted benzene.
5. How will you differentiate between the following pairs using IR spectra?
- (a) $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_2=\text{CHCH}_2\text{OH}$
- (b) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3CHO

Solution

(a) $\text{CH}_3\text{CH}_2\text{CHO}$ will show absorption band at $1740\text{--}1720\text{ cm}^{-1}$ for C=O group.
 $\text{CH}_2=\text{CHCH}_2\text{OH}$ will show the following absorption bands

- $\sim 1050\text{ cm}^{-1}$ for primary alcohols (C–O stretching and bending)
- At $3100\text{--}3000\text{ cm}^{-1}$, C=C str.
- At 905 cm^{-1} for vinyl group ($\text{H}_2\text{C}=\text{C}-\text{H}$) str.
- Band at $3200\text{--}3500$ for OH group.

(b) $\text{CH}_3\text{CH}_2\text{OH}$ will show the following bands.

- C–H str at $2960\text{--}2850\text{ cm}^{-1}$
- Band at $3300\text{--}3400\text{ cm}^{-1}$ due to OH group.
- CH_3CHO shows the following absorption bands
- Band at 1745 cm^{-1} due to C=O str.

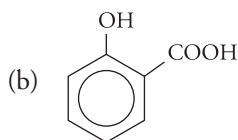
Practice problems

1. Give the characteristic absorption bands of the infrared spectrum in the following compounds.

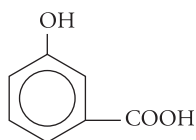
- | | |
|---------------------------------------|---|
| (a) n-octane | (b) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}=\text{CH}_2$ |
| (c) CH_3CHO | (d) CH_3COCH_3 |
| (e) $\text{C}_6\text{H}_5\text{NH}_2$ | (f) CH_3NH_2 (g) CH_3OH |

2. Differentiate between the following compounds on the basis of their IR spectra.

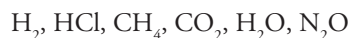
- (a) CH_3COOH and CH_3COCH_3



and



3. Which of the following molecules will show IR spectrum and why?



[Ans All except H_2 because it is homonuclear]

4. Where do the following absorb in the IR region?

(i) Primary aliphatic amine

(ii) Carbonyl in aliphatic aldehydes

(iii) OH in phenols

(iv) OH in carboxylic acids

17.5 Rotational Spectroscopy of Diatomic Molecules

The rotational spectra results from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region extending from 1 cm to 100 μm with an energy range of nearly 100 J/mol. The rotational energy is quantised which means that the rotational energy has certain permitted values known as rotational energy levels which may be calculated for any molecule.

Consider a diatomic molecule in which m_1 and m_2 are the masses of two atoms (assumed to be point masses) separated by a distance r , rotating about an axis passing through the centre of mass c . Let r_1 and r_2 be the distance of the two atoms from the centre of mass. The diatomic molecule is assumed to be a rigid rotor (i.e., it does not vibrate during rotation).

Although the point masses can rotate about three axes but for quantum (microscopic) objects rotation around the bond axis does not correspond to any change in the configuration of the molecule hence these point masses have two independent rotations with respect to the two axes passing through the centre of mass 'c' and perpendicular to the bond length.

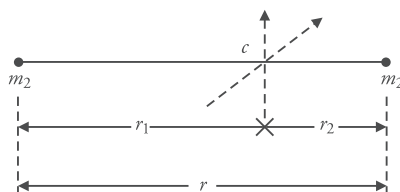


Figure 17.24 A rigid diatomic molecule rotating about its centre of mass

As the system is balanced about its centre of mass, we may write

$$m_1 r_1 = m_2 r_2 \quad (1)$$

Since the moment of inertia I is given by

$$I = \sum m r^2 \quad \text{Units of } I = \text{kg m}^2$$

$$\therefore I = m_1 r_1^2 + m_2 r_2^2 \quad (2)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 \quad (\text{Using equation 1})$$

$$= r_1 r_2 (m_1 + m_2) \quad (3)$$

$$\because r = r_1 + r_2 \text{ (from the figure 1)} \quad (4)$$

\therefore from eq (1) and eq (4)

$$m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$$

$$\text{hence } r_1 = \frac{m_2 r}{m_1 + m_2} \text{ and } r_2 = \frac{m_1 r}{m_1 + m_2}$$

Substituting the value of r_1 and r_2 in eq (2) we have

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_1^2 m_2 r^2}{(m_1 + m_2)^2} \quad (6)$$

$$= \frac{m_1 m_2 (m_1 + m_2) r^2}{(m_1 + m_2)^2} = \frac{m_1 m_2 r^2}{m_1 + m_2} = \mu r^2 \quad (7)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the molecule

Equation (7) gives the moment of inertia in terms of reduced mass μ at a distance r from the centre of mass c .

Rotational spectroscopy of linear rigid rotor molecules:

A diatomic molecule is assumed to be a linear rigid rotor, that is, its internuclear distance does not change during rotational motion.

The angular momentum L of a rotating molecule is given by $I\omega$ where ω is the angular (rotational) velocity in radians/s. Angular momentum is quantised and is given by

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \quad (8)$$

where $J = 0, 1, 2, 3 \dots$ termed as the rotational quantum numbers.

The energy E_J of a rotating molecule is given by

$$E_J = \frac{1}{2} I \omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad (9)$$

Substituting the value of L from Eq. (8)

$$E_J = J(J+1) \frac{h^2}{8\pi^2 I} \quad (10)$$

E_J = energy in joules

h = Planck constant = 6.626×10^{-34} J s

I = moment of inertia in kg m²

J = rotational quantum number

It is customary to express the energy difference between two rotational levels as wave number expressed in cm⁻¹. Wave number is the reciprocal of wavelength $\frac{1}{\lambda}$, hence on dividing Eq (10) by hc

$$\frac{E_J}{hc} = J(J+1) \frac{h}{8\pi^2 I c} \quad (11)$$

The equation can be further simplified by writing it in terms of rotational constant B , which is defined as

$$B = \frac{h}{8\pi^2 I c}$$

Units of B are wave number units, that is, cm⁻¹

Hence Eq. (11) reduces to

$$\frac{E_J}{hc} \text{ or } \bar{\nu} = B J(J+1) \text{ cm}^{-1} \quad (12)$$

Putting the value of $J = 0, 1, 2, 3$ in Eq. (12), the wave numbers for different rotational levels will be $0, 2B, 6B, 12B, 20B, 30B, \dots$ and so on.

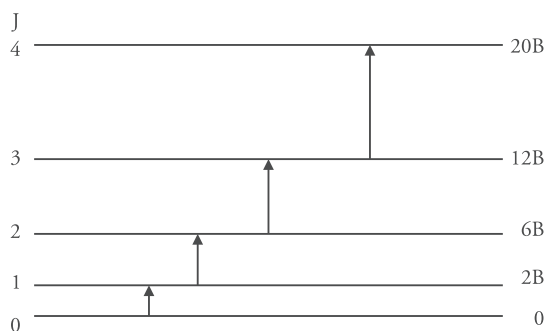


Figure 17.25 Rotational energy levels of a rigid diatomic molecule and the allowed transitions.

According to quantum mechanics the permissible transitions for a rigid rotator are those for which the difference in angular momentum is one. Hence the selection rule for a rotational transition is

$$\Delta J = \pm 1$$

This means that transitions can occur between rotational ground state ($J = 0$) and first excited state ($J = 1$) and vice versa or between levels $J = 1$ to $J = 2$ but transition cannot occur between $J = 0$ to $J = 2$.

Positive sign indicates absorption whereas negative sign indicates emission of radiation. In microwave spectroscopy usually absorption occurs; so $\Delta J = +1$. Suppose the transition occurs from J to $J + 1$, then rotational frequency is given by the equation

$$\begin{aligned}\bar{\nu}_{[J \rightarrow (J+1)]} &= B(J+1)(J+2) - BJ(J+1) \\ &= B[(J^2 + 3J + 2) - J^2 - J] \\ &= B(2J + 2) \\ &= 2B(J + 1) \\ \therefore \bar{\nu}_{[J \rightarrow (J+1)]} &= 2B(J + 1) \text{ cm}^{-1}\end{aligned}\quad (13)$$

$$\begin{array}{lll} J' = 0 & J'' = 1 & \bar{\nu}_{0 \rightarrow 1} = 2B \text{ cm}^{-1} \\ J' = 1 & J'' = 2 & \bar{\nu}_{1 \rightarrow 2} = 4B \text{ cm}^{-1} \\ J' = 2 & J'' = 3 & \bar{\nu}_{2 \rightarrow 3} = 6B \text{ cm}^{-1} \text{ etc.} \end{array}$$

(where J' is the lower transitional level read as J prime and J'' is the upper transitional level read as J double prime)

It is obvious from the above expression that the difference between the two consecutive rotational spectral lines is $2B$ as shown in Figure 17.26

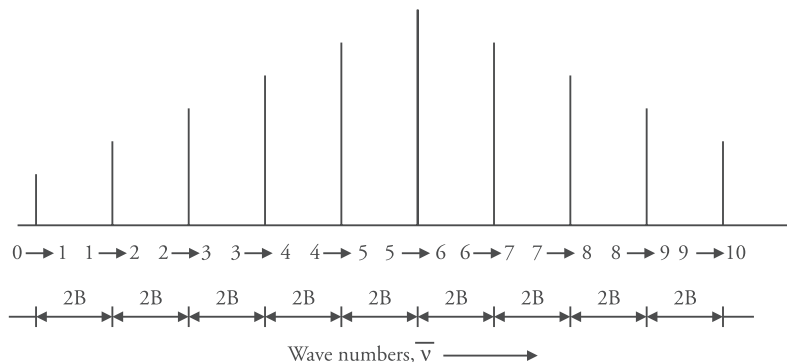


Figure 17.26 Appearance of a rotational spectrum

This is called the frequency separation or wave number separation. Thus the rotational spectral lines are equidistant.

Intensities of Rotational Spectral Lines

Although the rotational spectral lines are equally spaced but their intensities are not equal. The intensities increase with increasing J , pass through a maximum and then decreases as J increases further. The intensities of spectral lines depend upon the number of molecules in any energy level J . Greater the population of the energy level, greater is the number of molecules that can be promoted to the next higher level and hence greater is the intensity of absorption. Since the energy

level population is given by the Boltzmann distribution, the intensity of rotational spectral lines is also proportional to the Boltzmann distribution of molecules in the rotational energy levels, that is

$$\text{Intensity} \propto N_J / N_0 = e^{\frac{-E_J}{k_B T}}$$

where N_J and N_0 is the population of molecules in the higher and lower energy level and k_B is the Boltzmann constant.

In the absence of external field all the energy levels are degenerate so the intensity of spectral lines depends upon the degeneracy factor g_J . For a diatomic molecule the degeneracy factor

$$g_J = 2J + 1 \quad (15)$$

Taking the degeneracy factor into account, Eq. (14) can be rewritten as

$$\frac{N_J}{N_0} = g_J e^{\frac{-E_J}{k_B T}} \quad (16)$$

From Eq. (15), this can be further be written as.

$$\frac{N_J}{N_0} = (2J + 1) e^{\frac{-E_J}{k_B T}}$$

$$\text{or Intensity} \propto \frac{N_J}{N_0} = (2J + 1) e^{\frac{-E_J}{k_B T}}$$

$$\text{putting } E_J = \frac{hc}{\lambda} = hc\bar{\nu} = hcBJ(J + 1) \text{ where } \bar{\nu} = BJ(J + 1) \quad (\text{from Eq. 12})$$

$$\text{hence, } \frac{N_J}{N_0} = (2J + 1) e^{\frac{-BJ(J+1)hc}{k_B T}} \quad (17)$$

Figure 17.27 gives the plot of $\frac{N_J}{N_0}$ versus J for a diatomic molecule at room temperature.

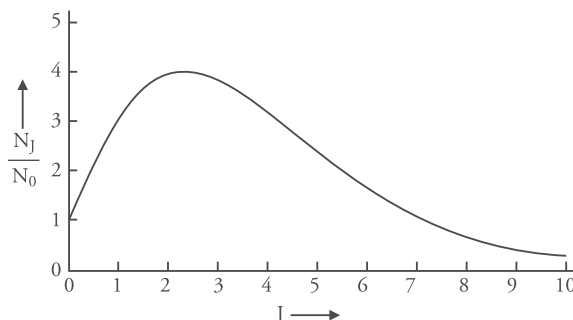


Figure 17.27 Plot of the relative Boltzmann population versus J for a diatomic molecule

The graph clearly shows that relative intensity passes through a maximum. The value of J corresponding to the maximum population is given by

$$J_{\max} = \left(\frac{k_B T}{2hcB} \right)^{\frac{1}{2}} - \frac{1}{2} \quad (18)$$

The J_{\max} should be rounded off to the nearest integral value.

The Non-Rigid Rotor Model

When a molecule rotates with great speed, it cannot be treated as a rigid rotator because there are distortions due to centrifugal and other forces. Considering the centrifugal distortion alone the rotational energies are modified as

$$E_J \text{ (in cm}^{-1}\text{) or } \bar{\nu} = BJ(J+1) - DJ^2(J+1)^2 \quad (19)$$

D is the centrifugal distortion constant

When transition occurs from J to $J+1$, the wave number of the line produced is given by

$$\begin{aligned} \Delta \bar{\nu} &= \bar{\nu}_{J+1} - \bar{\nu}_J \\ &= [B(J+1)(J+2) - D(J+1)^2(J+2)^2] - [BJ(J+1) - DJ^2(J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \\ &= 2(J+1)\{B - 2D(J+1)^2\} \end{aligned}$$

As J increases, the factor $[B - 2D(J+1)^2]$ decreases; hence $\Delta \bar{\nu}$ decreases with increase in the value of J .

Applications of Microwave Spectroscopy

For a diatomic molecule, the moment of inertia I can be calculated with the knowledge of frequency separation $\Delta \nu$ using the formula $B = h/8\pi^2 Ic$. If the masses of the two atoms in a diatomic molecule are known, then bond distance r can be calculated accurately using the formula

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2$$

Solved Example

1. For CO molecule the rotational spectral lines appear at 3.8424 cm^{-1} for the transition $J = 0$ to $J = 1$. Calculate the moment of inertia and bond distance for the molecule.

Solution

We know that

$$\bar{\nu}_{J \rightarrow (J+1)} = \bar{\nu}_{0 \rightarrow 1} = 2B$$

$$\text{Therefore } 2B = 3.8424 \text{ cm}^{-1}$$

$$\text{or } B = 1.9212 \text{ cm}^{-1}$$

Moment of inertial I :

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.624 \times 10^{-27}}{8 \times 3.14 \times 3.14 \times 1.9212 \times 3 \times 10^{10}}$$

$$I = 1.4567 \times 10^{-39} \text{ g cm}^2$$

$$= 1.4567 \times 10^{-46} \text{ kg m}^2$$

reduced mass of CO ,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\frac{12}{N_A} \times \frac{16}{N_A}}{\frac{12}{N_A} + \frac{16}{N_A}} = \frac{12 \times 16}{N_A(12 + 16)}$$

where N_A = Avogadro's number

$$\mu = \frac{12 \times 16}{6.023 \times 10^{23} \times 28} = 1.14 \times 10^{-23} \text{ g mol}^{-1} = 1.14 \times 10^{-26} \text{ kg mol}^{-1}$$

$$I = \mu r^2 \text{ or } r = \sqrt{\frac{I}{\mu}}$$

$$\begin{aligned} \text{Bond distance } r &= \sqrt{\frac{1.4567 \times 10^{-46}}{1.14 \times 10^{-26}}} = 1.13 \times 10^{-8} \text{ cm} \\ &= 1.13 \times 10^{-10} \text{ m} = 1.131 \text{ \AA} = 113 \text{ pm} \end{aligned}$$

2. The internuclear distance (bond length) of carbon monoxide molecule is 1.13 \AA . Calculate the energy (in joules and eV) of this molecule in the first excited rotational level. Also calculate the angular velocity of the molecule. Given atomic masses of $^{12}\text{C} = 1.99 \times 10^{-26} \text{ kg}$; $^{16}\text{O} = 2.66 \times 10^{-26} \text{ kg}$.

Solution

$$r = 1.13 \text{ \AA} = 1.13 \times 10^{-10} \text{ m}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.99 \times 10^{-26} \text{ kg} \times 2.66 \times 10^{-26} \text{ kg}}{1.99 \times 10^{-26} \text{ kg} + 2.66 \times 10^{-26} \text{ kg}} = 1.14 \times 10^{-26} \text{ kg}$$

moment of inertia $I = \mu r^2$

$$I = 1.14 \times 10^{-26} \text{ kg} \times (1.13 \times 10^{-10} \text{ m})^2 = 1.46 \times 10^{-46} \text{ kg m}^2$$

Energy of a rigid diatomic molecule is given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joule}$$

For the first excited level, $J=1$; hence

$$\begin{aligned} E_1 &= \frac{(6.626 \times 10^{-34})^2 \times 1(1+1)}{8 \times 3.14 \times 3.14 \times 1.46 \times 10^{-46} \text{ kg m}^2} \\ &= 7.61 \times 10^{-23} \text{ Joule} \end{aligned}$$

since $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

$$\begin{aligned} E_1 &= \frac{7.61 \times 10^{-23}}{1.602 \times 10^{-19} \text{ J eV}^{-1}} \\ &= 4.76 \times 10^{-4} \text{ eV} \end{aligned}$$

$$\text{angular velocity } \omega = \sqrt{\frac{2E_1}{I}} = \sqrt{\frac{2 \times 7.61 \times 10^{-23} \text{ J}}{1.46 \times 10^{-46} \text{ kg m}^2}} = 3.32 \times 10^{11} \text{ radians}^{-1}$$

Practice Problems:

1. The pure rotational (microwave) spectrum of gaseous HCl consist of a series of equally spaced lines separated by 20.80 cm^{-1} . Calculate the bond distance of the molecule. The atomic masses are $^1\text{H} = 1.673 \times 10^{-27} \text{ kg}$; $^{35}\text{Cl} = 58.06 \times 10^{-27} \text{ kg}$ [Ans 129 pm]
2. For a rigid diatomic molecule the rotational constant at 300 K is 1.566 cm^{-1} , calculate the value of J_{max} . [Ans 7.56 \approx 8]

17.6 Vibrational–Rotational Spectra for a Diatomic Molecule

Since the rotational energy is lesser than the vibrational energy, hence vibrational motion is accompanied by rotational motion and we obtain a vibrational–rotational spectra where the transitions between rotational energy levels and vibrational energy levels occur simultaneously (i.e., both v and J change). Treating the molecule as an anharmonic oscillator the selection rules are

$$\Delta v = \pm 1, \pm 2, \pm 3 \text{ and } \Delta J = \pm 1$$

$$\Delta J = 0 \text{ is not allowed.}$$

Figure 17.28 gives the vibrational rotational spectrum of a diatomic molecule.

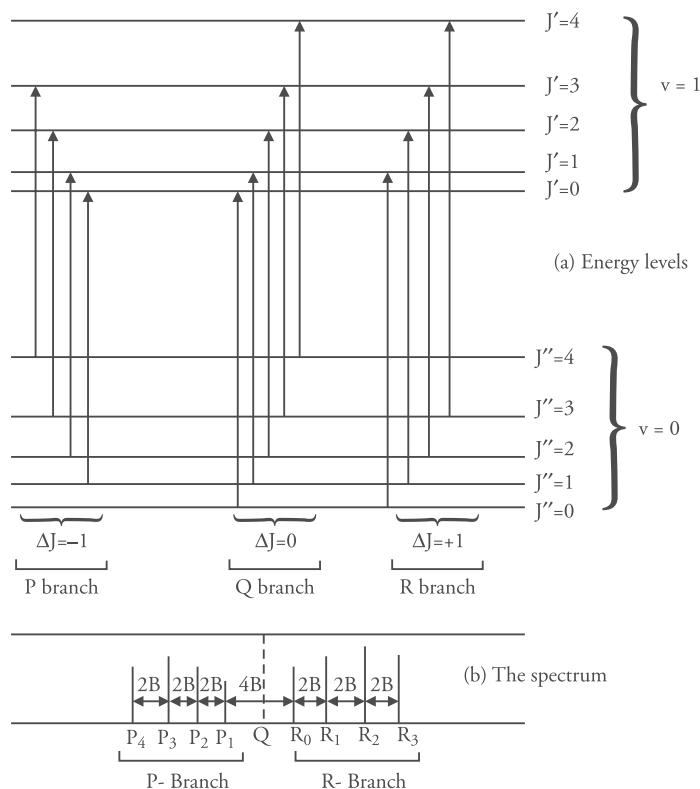


Figure 17.28 The vibrational rotational spectrum of a diatomic molecule

The spectra consists of equally spaced lines with spacing equal to $2B$ on each side of the band centre (Q). The spectral lines corresponding to $\Delta J = 0$ (forbidden) do not appear in the rotation vibration spectra (shown by dashed line Q in the spectra and termed as the band centre). The lines corresponding to $\Delta v = +1$ and $\Delta J = -1$ are called P branch are obtained at frequency lower than the fundamental frequency. Similarly lines corresponding to $\Delta v = 1$ and $\Delta J = +1$ are called R branch and appear at frequency higher than the fundamental frequency.

17.7 Nuclear Magnetic Resonance Spectroscopy

Introduction and theory

Like microwave, infrared and ultraviolet spectroscopy, nuclear magnetic resonance (NMR) spectroscopy is also a form of absorption spectroscopy. The sample absorbs electromagnetic radiations in the radiofrequency region. NMR spectrum is a plot of the frequencies of absorption peaks versus peak intensities.

To explain NMR spectroscopy, let us begin by describing the magnetic properties of the nuclei.

Magnetic properties of nuclei

- (i) **Nucleus—A tiny bar magnet** All nuclei carry a charge. These charged nuclei are considered to spin. The spinning nuclear charge generates a magnetic dipole along the axis (Fig. 17.29) so that these nuclei behave as tiny bar magnets having a magnetic moment μ .

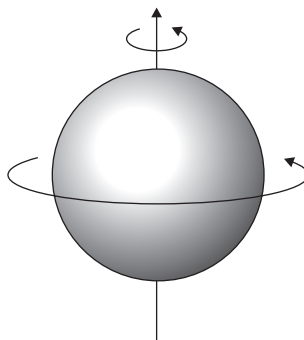


Figure 17.29 Spinning charge in proton generates magnetic dipole

- (ii) **Effect of external magnetic field** In the absence of an external magnetic field, the magnetic moments are randomly oriented. If the nucleus is placed in an external magnetic field, it can be oriented in different ways. According to quantum mechanics, $2I + 1$ orientations are possible where I is the spin quantum number of the nucleus. Hydrogen nucleus (proton) with the value of $I = \frac{1}{2}$ can have $2I + 1$, that is, $2 \times \frac{1}{2} + 1 = 2$ orientations with respect to the external magnetic field.

It can be aligned either

- (i) Parallel to the field (α spin) or
- (ii) Anti-parallel to the field (β spin)

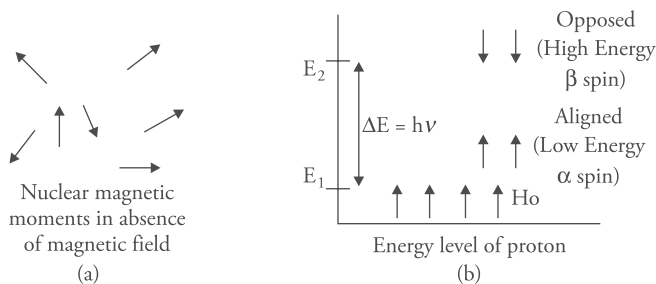


Figure 17.30 (a) Random orientation of magnetic moments in absence of magnetic field
(b) Magnetic moments aligned in the presence of external magnetic field

- (iii) **Precessional motion** The movement of the nucleus is like that of a spinning top. The top spins and also moves around slowly. Similarly, the nucleus also performs a waltz like motion; this waltz like motion of the nucleus along the vertical axis is known as the precessional motion (Fig. 17.31).

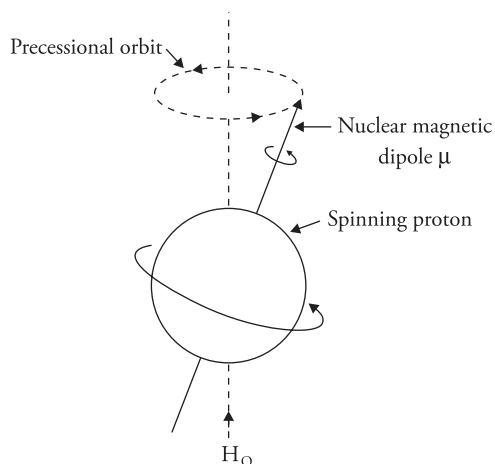


Figure 17.31 Proton precessing in a magnetic field H_0

As the proton is a spinning magnet, it precesses along the axis of the magnetic field with its orientation either along the external magnetic field or opposite to it. The orientation along the field has low energy and is stable, whereas the anti-parallel orientation has high energy. This energy difference ΔE between the two states is given by

$$\Delta E = 2\mu H_0 \quad (\text{i})$$

Applying Bohr's relation

$$\Delta E = h\nu \quad (\text{ii})$$

Relating Eq. (i) and (ii), we have

$$\nu = \frac{2\mu H_0}{h} \quad (\text{iii})$$

where

ν = frequency of the electromagnetic radiation

μ = magnetic moment of the spinning nuclei

H_0 = external field in Gauss

h = Planck's constant

It is possible to induce transition between the two states. On absorbing energy, a proton precessing in the aligned orientation can pass in anti-parallel orientation. This transition of a proton from

one orientation to another is called *flipping* of the proton. The proton can also return from higher energy state (antiparallel orientation β spin) to lower energy state (α spin) by losing energy.

The energy required to flip the proton from one state to another depends upon the strength of the external field. Stronger the external field, greater will be the tendency of the proton to remain aligned with the field and higher will be the frequency of radiation required to flip the proton to the higher energy state.

It is important to remember that the precessing proton will absorb energy only when the precessing frequency of the spinning nucleus is same as the frequency of the radiofrequency beam. When this occurs, the nucleus and the radiofrequency beam are said to be in resonance. For example in the field of 14092 Gauss, the energy required to cause flipping of the proton corresponds to the electromagnetic radiation of frequency 60 MHz.

NMR spectrometers are designed so that the radiofrequency is kept constant and the strength of the magnetic field is constantly varied. Now, at some value of the field strength, the energy required to flip the proton matches the energy of the radiation and absorption takes place. A signal is observed in the spectrophotometer. The spectrum so obtained is called the NMR spectrum. When the nucleus involved is the proton it is called PMR or *proton magnetic resonance*.

Spin active nuclei All nuclei do not exhibit NMR. Those nuclei which exhibit NMR phenomenon are called spin active nuclei. All nuclei possess spin angular momentum. Only those nuclei with spin quantum number I greater than zero will precess along the axis of rotation.

The spin quantum number I is associated with mass number and atomic number of the nuclei (Table 17.5). It is the resultant of the spins of a proton and a neutron.

Table 17.5 Spin quantum numbers

Mass number	Atomic number	Spin quantum numbers I
Odd	Odd or even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$
Even	Even	0
Even	Odd	1, 2, 3

Nuclei like ${}^{12}_6\text{C}$, ${}^{16}_8\text{O}$, ${}^{32}_{16}\text{S}$ with $I = 0$ are spin inactive. Nuclei ${}^1_1\text{H}$, ${}^{13}_6\text{C}$, ${}^{19}_9\text{F}$ are spin active and exhibit NMR spectroscopy.

Instrumentation

Nuclear magnetic resonance spectrophotometer consists of a magnet, a radiofrequency source, a detector and an amplifier (Fig. 17.32).

A brief description of the various components is as follows.

1. **Magnet** An electromagnet or a permanent magnet is used to supply the magnetic field H .
2. **Magnetic field sweep** It is used to vary the strength of the magnetic field. A pair of coils (Helmholtz coils) are used to bring this alteration. By varying a direct current through these coils, the effective field can be changed without loss of field homogeneity. The field change is synchronized with the linear drive of the chart recorder.

3. **Radiofrequency source** A signal from radiofrequency source ($\nu = 60 \text{ megacycles s}^{-1}$) is made to fall on the sample by feeding energy from the radiofrequency source into a coil around the sample tube.
4. **Sample holder** NMR sample cell consists of a glass tube which is placed between the pole faces of a magnet.
5. **Signal detector and recording system** The electric signal generated into the coil is amplified before it is recorded.

As the field strength increases, the precessional frequency of each proton increases until resonance with radiofrequency takes place. As the protons come to resonance, the signal from the detector is produced on the chart paper.

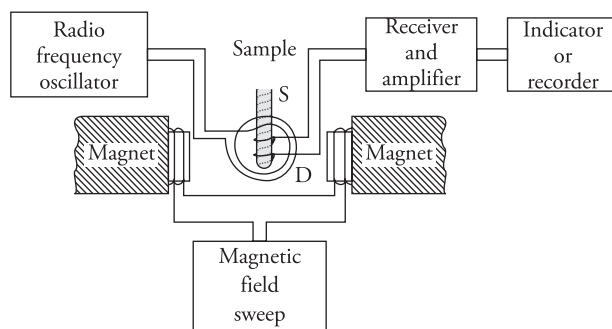


Figure 17.32 Schematic sketch of NMR spectrometer

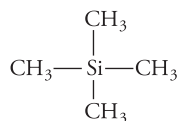
Chemical shift

If the resonance frequencies of all protons in a molecule were the same, they would all absorb at the same field strength and the spectrum would consist of a single signal. However, it is not so. The precessional frequency of all the protons in the same external magnetic field is not the same. The frequency at which a proton absorbs depends upon the magnetic field that the proton feels or experiences. This in turn depends upon the environment of the proton, electron density around the proton, presence of nearby protons and various other factors.

When a molecule is placed in an electric field, the electrons rotating around it generate their own electric field. This induced magnetic field may align with the applied field or may oppose it. If it aligns with the applied field, the proton feels a higher field strength and is said to be *deshielded*. If the induced magnetic field opposes the applied field, the proton experiences a lesser magnetic field and is said to be *shielded*. Shielding shifts the absorption up field and deshielding shifts the absorption down field to get an effective field strength necessary for absorption.

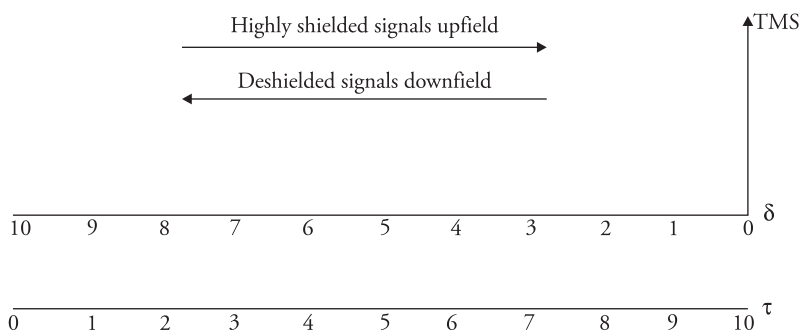
Such shifts in the position of NMR spectrum (as compared to a standard reference) which arise due to the shielding and deshielding of proton by the electrons are called *chemical shifts*.

Measurement of chemical shift It is extremely difficult to measure the precessional frequency of a group of nuclei in absolute frequency units. The relative absorption frequency is measured using a suitable standard. The standard used universally to measure chemical shift is tetramethylsilane (TMS).



Tetramethylsilane (TMS)

TMS has 12 equivalent protons and hence a sharp single signal is obtained. Owing to the low electronegativity of silicon, the shielding of equivalent protons in tetramethylsilane is greater than most organic compounds. The NMR signal of TMS is taken as reference and the signals of other compounds are measured relative to it. *This difference in the absorption position of the proton with respect to TMS signal is called chemical shift* (Fig. 17.33).

**Figure 17.33** Chemical shift

TMS is chosen as a reference because it is miscible with most organic solvents and is volatile hence can be easily removed from the system. It also does not take part in intermolecular associations with the sample.

The chemical shifts of various protons are shown in Table 17.6.

Units used in NMR

Chemical shift positions are usually expressed in δ (delta) units. The value of δ is expressed in parts per million (ppm). The δ units is proportionality and is thus dimensionless.

The value of δ for a substance with respect to TMS is obtained by measuring the resonance frequency of the sample ν_s and the resonance frequency of TMS ν_{TMS} .

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{operating frequency in megacycles}} = \frac{\Delta\nu}{\text{operating frequency in megacycles}}$$

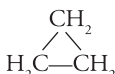
$\Delta\nu$ = frequency shift

Most organic compounds resonate at lower field than the protons of TMS. Hence, the value of δ for TMS is arbitrarily fixed at zero and the protons absorbing at a lower field are assigned positive values from 0 to 10. The TMS signal appears at the extreme right of the spectrum at $\delta = 0$ ppm. Greater the deshielding of the proton, larger will be the value of δ .

Another scale for measurement is the τ (tau) scale. TMS is arbitrarily assigned a value of 10 ppm on the τ scale. The two scales are related as follows

$$\tau = 10 - \delta$$

Table 17.6 Types of protons and chemical shift in ppm

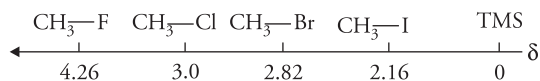
Types of protons			Chemical shift in ppm	
			δ	τ
(i)	Cyclo-propane		0.2	9.8
(ii)	Primary	R—CH ₃	0.9	9.1
(iii)	Vinylic	C=C—H	4.6 – 5.8	5.4 – 4.2
(iv)	Acetylenic	C≡C—H	2 – 3.5	8 – 6.5
(v)	Aromatic	Ar—H	6 – 9.0	4 – 1.0
(vi)	Fluorides	H—C—F	4 – 4.5	6 – 5.5
(vii)	Chlorides	HC—Cl	3 – 4	7 – 6
(viii)	Alcohols	H—C—OH	3.4 – 4	6.6 – 6
(ix)	Ethers	H—C—OR	3.3 – 4	6.7 – 6
(x)	Esters	H—C—COOR	2 – 2.2	8 – 7.8
(xi)	Acids	H—C—COOH	2 – 2.5	8 – 7.5
(xii)	Aldehydic	RCHO	9 – 10	1 – 0
(xiii)	Hydroxy	R—OH	1 – 5.5	9 – 4.5
(xiv)	Phenolic	Ar—OH	4 – 12	6 to –2
(xv)	Enolic	C=C—OH	15 – 17	–5 to –7
(xvi)	Carboxylic	RCOOH	10.5 – 12	–0.5 to –2

Factors influencing the chemical shift

Shielding and deshielding effects Shielding and deshielding has been discussed earlier (refer to chemical shift). Let us now discuss the factors affecting chemical shift.

- (i) **Inductive effect** The $-I$ effect of groups causes reduction in electron density around the proton (deshielding). Thus, a smaller field is needed to bring about resonance. Hence, the absorption occurs downfield (higher the δ values) far from the TMS signal.

The effect of electronegativity on the chemical shift is illustrated below.



Similarly, an electropositive atom like silicon pushes the electrons towards the methyl group. Hence, the methyl groups are highly shielded and a higher field is needed to bring about resonance. Thus, the absorption occurs upfield (lower δ value) which has arbitrarily been assigned the value of zero.

- (ii) **Anisotropic effects** Shielding and deshielding in unsaturated compounds depends upon the manner in which the π electrons circulate under the influence of the applied field. These

effects are diamagnetic (opposed to the field) in certain directions and paramagnetic (aligned with the field) in other; hence, these effects are called anisotropic effects.

Alkenes The alkene is so oriented that the plane of the double bond is at right angles to the field. Circulation of π electrons induces a magnetic field which is diamagnetic (opposed to the field) around the carbon atom and paramagnetic (along the field) in the region of the alkene protons (Fig. 17.34). Thus, the protons will feel greater field strength and require lesser external magnetic field to exhibit resonance and hence, the absorption occurs at a lower field (higher δ value) than expected in absence of this effect.

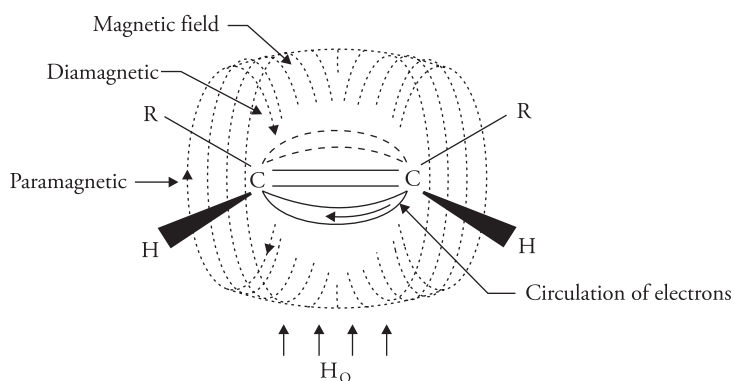


Figure 17.34 Induced anisotropic magnetic field around an alkene group

Alkynes The orientation of electrons around the triple bond is such that the protons experience diamagnetic shielding effect (Fig. 17.35). Thus, the protons feel smaller field strength (shielding) and hence require more external magnetic field to come to resonance. Therefore, the absorption occurs at higher field (low δ value).

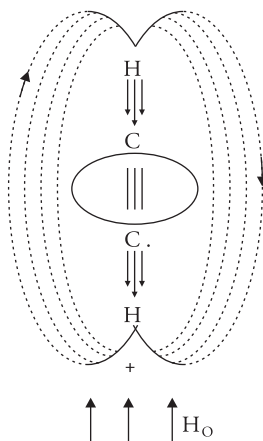


Figure 17.35 Shielding of acetylene protons

Benzene In the presence of the external magnetic field, the π electrons of the benzene ring circulate to produce a ring current (Fig. 17.36). Aromatic rings show strong anisotropy. The induced current is diamagnetic (opposes the applied field) in the centre of the ring and paramagnetic (aligned with the field) outside the ring. Thus, the aromatic protons (around the periphery of the ring) are deshielded and absorb down field (higher δ values). It is important to note that the protons held above and below the plane of the ring are shielded and resonate at low δ values.

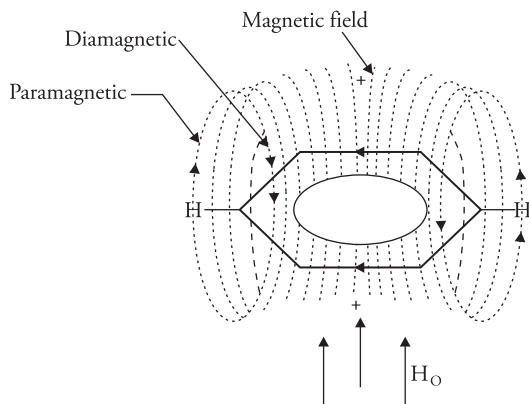


Figure 17.36 Anisotropic effects in benzene

Carbonyl compounds In carbonyl compounds, the magnetic field induced by π electrons in the region of the protons is oriented in the same direction as the applied field. The protons are deshielded and a smaller magnetic field is required to bring about resonance and hence they absorb downfield (higher δ values).

Table 17.7 gives the approximate chemical shift ranges for protons attached to anisotropic groups.

Table 17.7 Chemical shift due to anisotropic effects

Compound	Shielding /Deshielding effect	Absorption	δ value
Alkene	Deshielding	Lower field	High (5 – 6)
Alkyne	Shielding	Higher field	Low (1.5 – 3.5)
Aromatic	Deshielding (Protons attached to the ring)	Lower field	High (7 – 8)
Carbonyl	Deshielding	Lower field	High (9.5 – 10.0)

(iii) **Hydrogen bonding**

Hydrogen bonded proton is attached to a strongly electronegative atom and hence is highly deshielded. Therefore, the absorption occurs downfield (high δ value). The extent of the downfield shift depends upon the strength of the hydrogen bonding. Greater the degree of hydrogen bonding, greater would be the downfield shift.

The approximate chemical shift position for various protons is given in Figure 17.37.

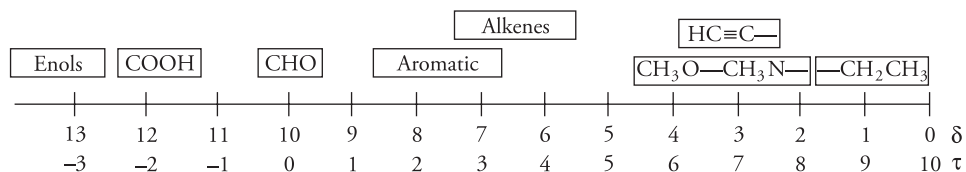
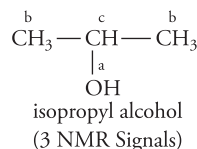
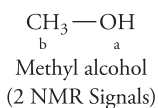
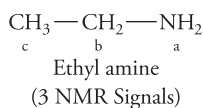
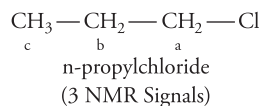
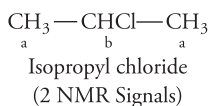
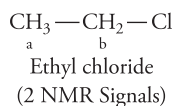
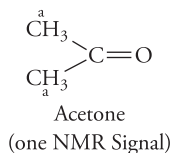
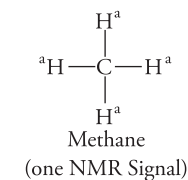


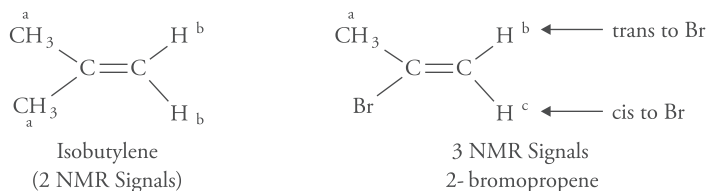
Figure 17.37 Approximate chemical shift positions for protons in organic molecules

Number of signals**Equivalent and non-equivalent protons**

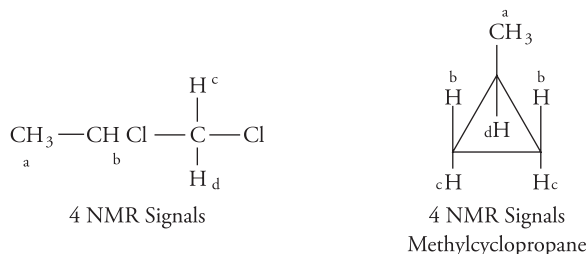
A set of protons with the same environment are said to be equivalent. Equivalent protons absorb at the same applied field strength and give one signal. Protons with different environments absorb at different field strengths and give different signals. The number of signals in an NMR spectrum tell us the number of different sets of equivalent protons. It must be remembered that magnetically equivalent protons are chemically equivalent. Equivalent protons are designated with the same letter.



It is important to note that chemically equivalent protons must also be stereochemically equivalent. For example,



Similarly 1,2-dichloropropane $\text{CH}_3\text{—CH}(\text{Cl})\text{—CH}_2\text{Cl}$ gives four signals because the two hydrogen attached to C_1 are not same.



Practice problems

- Predict the number of NMR signals in the following compounds.

(i) tert-butylamine	(ii) 1,2-dibromoethane
(iii) 1,1-dibromoethane	(iv) Ethylbenzene
(v) Mesitylene	(vi) Diethylether
(vii) 2-chloropropene	(viii) Propanal
(ix) Ethoxyacetic acid	(x) Propyl formate

[Ans (i) 2 (ii) 1 (iii) 2 (iv) 3 (v) 2 (vi) 2 (vii) 3 (viii) 3 (ix) 4 (x) 4]

Peak area and Proton counting

The following information is obtained from the NMR spectra.

- The number of signals gives the number of sets of equivalent protons.
- Peak area tells us about the number of protons in each equivalent set present in the compound.

The area under an NMR signal is directly proportional to the number of protons giving rise to the signal. Quantum energy is absorbed by the proton for flipping. The larger the number of equivalent protons, greater will be the energy absorbed and greater is the area under the absorption peak.

To find the number of protons in each equivalent set, the number of squares under each peak is counted and from this, the ratio of various kinds of protons is found. These ratios are then converted into a whole number. These whole numbers (or their multiples) tell us the number of protons represented by each signal.

Let us illustrate the above by considering the NMR spectra of toluene (Fig. 17.38).

The spectrum has two signals which indicate that the compound contains two set of equivalent protons. On counting the number of squares under each peak, it is found that the ratio of the

number of squares under the two peaks is 5 : 3. Thus, in toluene, the ratio of two equivalent sets of protons is 5 : 3. (5 protons of one kind and 3 of another kind)

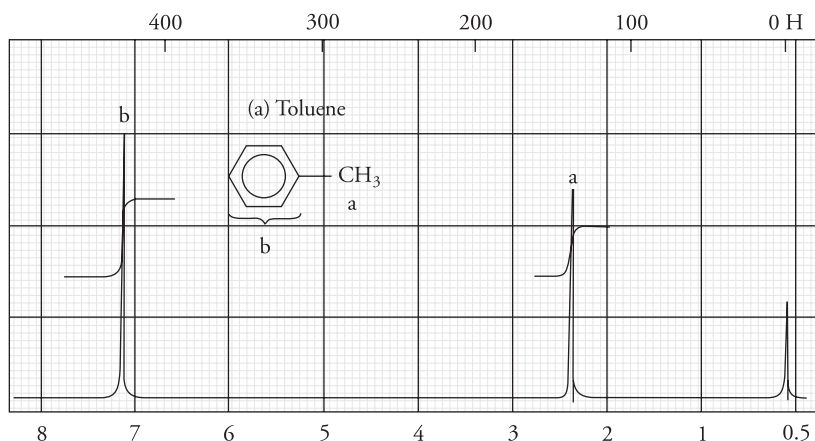


Figure 17.38 Spectra of toluene

Splitting of signals

Each signal in an NMR spectrum represents one set of equivalent protons. It is found that generally, the signals do not appear as singlets (single peak) but as multiplets (group of peaks). Consider the example of ethyl bromide $\overset{b}{\text{CH}_3}\overset{a}{\text{CH}_2}\text{Br}$. (Fig. 17.39). It has two sets of equivalent protons and hence two signals are expected. However, it has been observed that the two signals do not appear as single peaks (singlets), rather for *a* kind of protons ($-\text{CH}_2-$), a quartet (group of four peaks) and for *b* kind of protons ($-\text{CH}_3$), a triplet (group of three peaks) are noticed. Thus, in general it can be said that a set of *n* equivalent protons splits a signal due to neighbouring protons into a group of (*n*+1) peaks (multiplet).

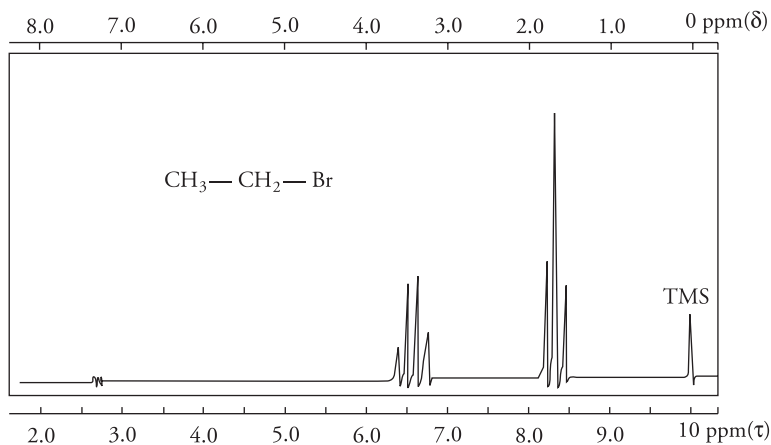


Figure 17.39 NMR spectrum of ethyl bromide

The splitting of a signal into multiplet is explained by spin–spin coupling between neighbouring protons.

Spin–spin coupling

The multiplicity of a signal is related to the number of protons in the neighbouring groups. To understand it properly, let us consider the example of ethyl bromide ($\text{CH}_3^{\text{b}}\text{CH}_2^{\text{a}}\text{Br}$). The spins of the two $-\text{CH}_2-$ protons can couple with the adjacent methyl protons in three different ways relative to the external field. The three different alignments of protons of the CH_2 groups are

(i)	$\uparrow\uparrow$	(Reinforcing)	↑ External field
(ii)	$\uparrow\downarrow \downarrow\uparrow$	(Not affecting)	
(iii)	$\downarrow\downarrow$	(Opposing)	

Thus, a triplet of peaks with intensities 1 : 2 : 1 is observed which corresponds to the distribution ratio of the alignment.

Similarly, the spins of CH_3 protons are aligned as follows.

(i)	$\uparrow\uparrow\uparrow$	(Strongly reinforcing)	↑ External field
(ii)	$\uparrow\uparrow\downarrow \uparrow\downarrow\uparrow \downarrow\uparrow\uparrow$	(Weakly reinforcing)	
(iii)	$\downarrow\downarrow\uparrow \downarrow\uparrow\downarrow \uparrow\downarrow\downarrow$	(Weakly opposing)	
(iv)	$\downarrow\downarrow\downarrow$	(Strongly opposing)	

Thus, the CH_2 signal appears as a quartet with intensity ratio 1 : 3 : 3 : 1.

The relative intensities of different signals can be obtained by the use of Pascal's triangle, where each coefficient terms is the sum of the two terms diagonally above it.

Number of neighbouring protons	(Number of peaks multiplicity, $n + 1$)	Intensity distribution
0	1	1
1	2	1 1
2	3	1 2 1
3	4	1 3 3 1
4	5	1 4 6 4 1
5	6	1 5 10 10 5 1

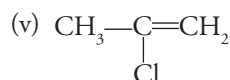
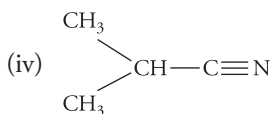
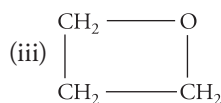
It may be noted that no splitting occurs if

- Protons are equivalent. For example, benzene gives a singlet.
- A set of equivalent protons do not have another set of equivalent protons attached to it.

For example, in $\text{CH}_3^c\text{CH}_2^b\text{OCH}_3^a$, the peak of *a* appears as a singlet as it is attached to the oxygen atom and has no protons adjacent to it. The signal of CH_2 appears as a quartet and CH_3 appears as a triplet.

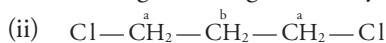
Solved examples

1. Predict the number of signals and multiplicity of the respective signals in the following compounds.

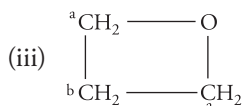


Solution

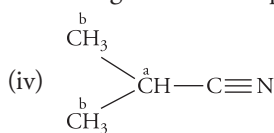
- (i) One signal Singlet as all hydrogens are equivalent



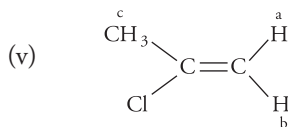
2- signals; signal of CH_2 (b) appears as a quintet (5 peaks $n+1$ rule; $4+1=5$ and that of CH_2 (a) protons as a triplet ($n+1$ rule; $2+1=3$)



2- signals A four proton triplet and a two proton quintet (5 peaks)



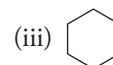
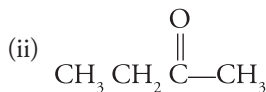
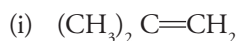
2- signals A six proton doublet and a one proton septet



3- signals H_a and H_b cause splitting of signals and each appears as a doublet. CH_3 appears as a singlet.

Practice problems

Predict the number of signals and multiplicity of the respective signals in the following compounds





[Ans (i) 2 signals; both singlets (6H, 2H); (ii) 3 signals; a three proton singlet, a two proton quartet, a three proton triplet; (iii) singlet (6H); (iv) 4 signals; singlet (1H), triplet (2H), sextet (2H), triplet (3H); (v) 3 signals; triplet (2H), triplet (3H), sextet (2H)]

Applications of NMR spectroscopy

Identification of structures of organic compounds

NMR spectroscopy is an important tool for predicting the structure of organic compounds. The following points are to be noted.

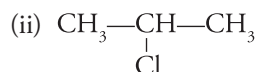
- Number of signals gives the number of equivalent protons
- Splitting of signals specifies the number of neighbouring protons.
- Position of the signals gives an insight of the functional groups, their position, presence or absence of hydrogen bonding, etc.

Let us consider few examples

NMR spectroscopy can differentiate between the following isomers.



(a)



(b)

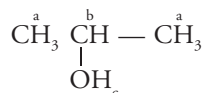
Isomer (a) gives three signals whereas (b) gives only two signals. The three signals of (a) are as follows.

- (i) A three proton triplet (CH_3)
- (ii) A two proton sextet ($-\text{CH}_2-$)
- (iii) A two proton triplet ($-\text{CH}_2\text{Cl}$)

The signals of (b) will appear as follows.

- (i) Doublet (6 H)
- (ii) Septet (1H) down field

Similarly, a distinction between 1-propanol and 2-propanol can be made.



1-propanol gives four signals

- | | | | |
|-----|---------|-------|---------------------------|
| (a) | Singlet | (1 H) | ↑
δ Value
increases |
| (b) | Triplet | (2H) | |
| (c) | Sextet | (2 H) | |
| (d) | Triplet | (3 H) | |

2-propanol gives three signals

(a)	Doublet	(6 H)	δ Value increases ↓
(b)	Septet	(1 H)	
(c)	Singlet	(1 H)	

Q2 A compound has the molecular formula $C_{10}H_{14}$. It gives the following NMR data.

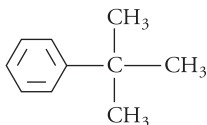
- (i) 0.88δ (9 H singlet)
- (ii) 7.28δ (5 H, singlet, aromatic protons)

Assign structure to the compounds

Solution

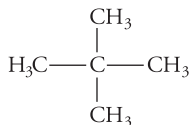
- (i) A nine proton singlet at 0.88δ indicates the presence of a tertiary butyl group.
- (ii) Five proton singlet at 7.28δ confirms phenyl ring.

Hence the structural formula of the compound may be



Q3 The following compounds show only one signal in the NMR spectrum. Write their structural formulae

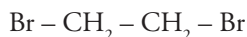
- (a) C_5H_{12} (b) C_2H_6O (c) $C_2H_4Br_2$ (d) C_4H_6
- (a) C_5H_{12} Single signal means that all the 12 hydrogen atoms are equivalent. Hence, the molecule contains four equivalent methyl groups. Hence its structure is



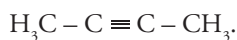
- (b) C_2H_6O Single signal can be accounted for by two equivalent CH_3 groups. Hence, the structure is



- (c) $C_2H_4Br_2$ It will have two equivalent methylene groups. Hence the probable structure is



- (d) C_4H_6 Single signal can be explained by considering that the molecule has two methyl groups and the two carbon atoms are without hydrogen.



Magnetic Resonance Imaging

One of the biggest applications of NMR spectroscopy is in the field of radiology, the magnetic resonance imaging (MRI). MRI uses the magnetic field and radiofrequency to find out the abnormalities in the tissue molecules. Human body is composed of nearly 70% water. MRI relies upon the magnetic properties of hydrogen atom in water to produce images.

The components of an MRI system are:

- Primary magnet
- Gradient magnets
- Radiofrequency (RF) coils
- Computer system.

Primary magnet: It is used to generate the external static magnetic field B_0 . In the absence of external magnetic field the protons are randomly oriented. An external magnetic field of 1.5 – 3 Tesla is generally applied in clinical MRI systems to align the protons either parallel or antiparallel to the primary magnetic field. Since the protons with parallel spin have low energy, a greater proportion of protons align parallel to the field. This is termed as longitudinal magnetisation and is oriented in the patients long axis or the z-axis.

The protons spin along the long axis of the primary magnetic field. This is called precession.

The precession rate is termed as the Larmor frequency $\omega_0 = \frac{\gamma B_0}{2\pi}$ where γ is the gyromagnetic ratio, that is, the ratio of magnetic moment of a spinning charged particle to its angular momentum. The Larmor frequency ω_0 is 42.57 MHz/Tesla for a proton and for an external magnetic field of 1.5 T the proton precesses at a radiofrequency of 63.9 MHz.

Gradient magnets: Once the subject is in the external magnetic field there is net magnetisation aligned along the field which is constant and hence no signal will be produced. Gradient magnets of lower magnetic field strength are used to create a variable field. These gradient coils generate secondary magnetic fields along the x-, y- and z-axes. They alter the precessing frequency and allow spatial encoding for MRI images in the x-, y- and z-axis.

Radiofrequency coils (RF coils): The RF coils produce radiofrequency pulse and when this is equal to the precessional frequency of the protons they absorb energy from the radiowave and some low energy protons flip to high energy state (a phenomenon called resonance) thereby decreasing the longitudinal magnetisation. The protons do not point in random directions anymore; they become synchronised and precess in phase turning the net magnetisation vector towards the transverse plane, that is, at right angles to the primary magnetic field.

When the RF coil is turned off the excited protons return to their original state. This is called *relaxation* and is measured in two directions

- Longitudinal (T_1): parallel to the external magnetic field B_0 (z-axis)
- Transverse (T_2): perpendicular to the external magnetic field (x-y axis)

T_1 relaxation: It is the process in which several protons flip back to their lower energy state parallel to the primary magnetic field B_0 along the z axis, giving their excess energy to the surrounding lattice. Hence it is called spin-lattice relaxation. The T_1 relaxation time depends upon the tissue composition and structure. The T_1 relaxation for water molecules takes a longer time.

T_2 relaxation: After turning off the RF pulse the protons that were in phase begin to dephase out of the Larmor frequency in the transverse (xy) axis. There is exchange of energy among the neighbouring spins and hence it is called spin–spin relaxation. This results in the reduction in transverse magnetisation which decreases with time.

In reality the spins dephase much quicker than T_2 because of inhomogeneities in the magnetic field B_0 .

T_2^* relaxation: T_2^* relaxation is the dephasing of proton due to factors like

- Magnetic interactions among neighbouring molecules
- Inhomogeneities in the external magnetic field B_0 .

T_2^* relaxation varies between tissues.

The net magnetic vector is the sum of longitudinal and transverse magnetisation. It spirals around the z axis with net precession. The changing magnetic moment vector results in free induction decay (FID) which induces an electric signal which is received by the RF coil.

Computer system: It receives the RF signal and converts the analog signal into a digital signal which is sent to the image processor where a mathematical calculation FTIR is performed and the image is displayed on the monitor.

Applications of MRI: This technique has a large number of medical applications which involve the diagnosis of cancer, soft tissue damage and various neurological problems.

17.8 Raman Spectroscopy

The spectroscopic techniques studied so far, electronic, rotational and vibrational involve absorption of light, but unlike other techniques Raman spectroscopy is based on the principle of scattering of light. When a beam of monochromatic radiation is passed through a substance (solid, liquid or gas) it may be absorbed, scattered or transmitted. If the frequency of the incident and scattered light is the same, it is called *elastic scattering or Rayleigh scattering*. Indian physicist C.V. Raman of Calcutta university in 1928 observed that some of the scattered light has discrete frequencies above and below the frequency of incident light. This was called *inelastic scattering or Raman scattering*. The Raman effect can be explained both by the classical theory and the quantum theory. Let us discuss them one by one.

Classical Theory of Raman Effect

As studied earlier in other spectroscopic techniques those incident radiations are absorbed which obey the Bohr's law $\Delta E = h\nu$. A molecule exhibits vibrational or rotational spectroscopy if it has either a permanent dipole moment or undergoes a change in dipole moment. The Raman effect is explained by considering the polarisability of the molecule. Polarisability is the ease with which an electron cloud can be distorted. When a molecule is placed in a static electric field its electron cloud is attracted towards the positive pole and the nucleus is attracted towards the negative pole of the electric field. The molecule becomes unsymmetrical (and is said to be polarised) and due to the separation of charge centres there is an *induced dipole moment* in the molecule. The magnitude of the induced dipole moment depends upon two factors

- Magnitude of applied electric field E
- Polarisability of the molecule.

$$\mu_{\text{ind}} = \alpha E \quad (1)$$

where α is the polarisability of the molecule. Polarisability is anisotropic, that is, it is not the same in all directions. In a linear diatomic molecule like H_2 the electrons forming the bond are displaced easily along the bond axis rather than across it. Hence the polarisability is greater along the bond axis rather than in the direction perpendicular to the internuclear axis. The anisotropic effect can be represented by drawing a polarisability ellipsoid (Fig. 17.40).



Figure 17.40 (a) H_2 molecule with end-on orientation (b) H_2 molecule with sideways orientation

When a beam of radiation falls on a sample of diatomic molecules, the electric field experienced by each molecule at a particular time is given by

$$E = E_0 \sin 2\pi \nu t \quad (2)$$

where E_0 is the amplitude of the vibrating electric field vector and ν is the frequency of incident radiation. Placing the value of E from Eq. (2) in Eq. (1) we have

$$\mu_{\text{ind}} = \alpha E_0 \sin 2\pi \nu t \quad (3)$$

According to the electromagnetic theory an oscillating dipole emits radiation whose frequency is the same as its oscillating frequency so the dipole moment oscillates at a frequency same as that of the applied field. This offers the classical explanation of Rayleigh scattering.

If apart from oscillation a molecule undergoes internal motion like rotation or vibration periodically that changes polarisability then the oscillating dipole will have superimposed upon it the vibrational or rotational oscillation. Hence the frequency of the scattered radiation will be either greater than or less than the frequency of the incident radiation. If the frequency of scattered radiation is lower than the frequency of the incident radiation it is called *Stokes radiation* and if it is higher than it is called the *Antistokes radiation*.

Selection Rule: For a molecular vibration or rotation to be Raman active it should undergo a change in molecular polarisability. Homonuclear diatomic molecules like H_2 , N_2 , O_2 , which are IR inactive as they do not have a permanent dipole moment, are Raman active since their vibration is accompanied by a change in polarisability of the molecule. As a result of this polarisability,

there occurs a change in the vibrational frequency. The selection rule for the vibrational Raman spectrum of a diatomic molecule is

$$\Delta v = \pm 1 \quad (4)$$

Quantum Theory of Raman Scattering

If photons of frequency ν and energy $h\nu$ falls on a molecule they undergo elastic or inelastic collisions with the molecule. In elastic collision there is no exchange of energy and the energy (and also frequency) of the incident and scattered radiation will be the same (Rayleigh scattering). If the collision is inelastic the molecule either gains energy from the photon or loses energy to the photon. If it gains energy ΔE from the photon then the energy of scattered photon will be $h\nu - \Delta E$ and its frequency will be $\nu - \Delta E/h$ where h is the Planck's constant.

If however the molecule loses energy ΔE to the photon, the energy of scattered photon will be $h\nu + \Delta E$ and the scattered frequency will be $\nu + \Delta E/h$. Radiations scattered with frequency lower than incident radiation is Stokes radiation and one with higher frequency is the antistokes radiation.

Pure rotational Raman spectra for diatomic molecules

The selection rule for pure rotational Raman spectrum of a diatomic molecule is

$$\Delta J = 0, \pm 2 \quad (5a)$$

The operative part of the rotation selection rule is

$$\Delta J = +2 \quad (5b)$$

Since $\Delta J = 0$ corresponds to Rayleigh scattering and $\Delta J = -2$ can be ignored as the rotational quantum number of the upper state must be greater than that of the lower state.

The rotational energy for a rigid diatomic rotor is given by the expression

$$F(J) = BJ(J+1)\text{cm}^{-1} \quad (J = 0, 1, 2, 3, \dots) \quad (6)$$

The centrifugal distortions are not considered here. Energy difference between the excited and ground state is given by

$$\begin{aligned} \Delta E &= F(J+2) - F(J) \\ &= B(J+2)(J+2+1) - BJ(J+1) \\ &= B(4J+6) \text{ cm}^{-1} \end{aligned} \quad (7)$$

The $\Delta J = +2$ transitions are called s-branch lines by convention. Thus

$$\Delta F(J) = B(4J + 6) \text{ cm}^{-1} \quad (J = 0, 1, 2, 3, \dots) \quad (8)$$

where J is the rotational quantum of the lower rotational energy level. Hence Raman spectral lines appear at the wave numbers given by the equation

$$\bar{\nu}_s = \bar{\nu}_{exc} \pm \Delta F(J) = \bar{\nu}_{exc} \pm B(4J+6) \text{ cm}^{-1} \quad (9)$$

$\bar{\nu}_{exc}$ is the incident frequency that causes excitation. The negative sign refers to the Stokes lines and the positive sign refers to the anti-stokes lines.

Figure 17.41 shows the energy level diagram and rotational Raman spectrum for a diatomic molecule. The figure shows that the first Stokes or first anti-stokes lines appear at a distance of $6B$ from the Rayleigh line. This is because on substituting $J=0$ in Eq. (8) one gets $6B$. The separation of the successive Raman lines is $4B$ which can be verified by putting the value of $J = 1, 2, 3$, in Eq. (9).

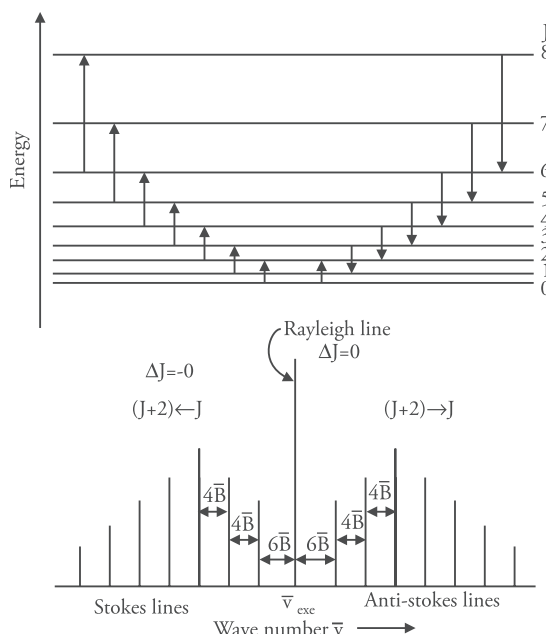


Figure 17.41 Rotational Raman spectrum of a rigid diatomic molecule

Instrumentation

Intense source of monochromatic radiation is used. Earlier mercury vapour lamps were used which gave intense monochromatic radiation at 4358 \AA (i.e., 435.8 nm). However, these days lasers are used as powerful source of monochromatic radiation. The light source falls on the sample and the

scattered light is observed at right angles to the direction of incident radiation. The detector used is either a photographic plate or a photomultiplier.

The frequency shifts called Raman shifts are expressed in wave numbers $\bar{\nu}$ in cm^{-1} . It is given by

$$\bar{\nu} \left(\text{in cm}^{-1} \right) = \frac{10^8}{\lambda \left(\text{in A}^0 \right)}$$

Hence Raman shift is given by

$$\Delta \bar{\nu}_{\text{Raman}} \left(\text{in cm}^{-1} \right) = \frac{10^8}{\lambda_{\text{exc}} \left(\text{in A}^0 \right)} - \frac{10^8}{\lambda_{\text{Raman}} \left(\text{in A}^0 \right)}$$

where λ_{exc} is the wavelength of the incident (exciting) radiation.

Applications:

- Raman spectroscopy is used to investigate various problems in chemistry like electrolytic dissociation, hydrolysis, etc.
- It is used for structure elucidation of organic and inorganic compounds, calculation of force constant, moment of inertia and bond lengths.

Solved Examples

1. A sample was irradiated by 4358 Å line of mercury. A Raman line was observed at 4452 Å. Calculate
 - (a) Raman shift in cm^{-1}
 - (b) The wavelength at which antistoke line would appear in the Raman spectrum.

Solution

$$\begin{aligned} \text{(a) } \Delta \bar{\nu}_{\text{Raman}} \left(\text{in cm}^{-1} \right) &= \frac{10^8}{\lambda_{\text{exc}} \left(\text{in A}^0 \right)} - \frac{10^8}{\lambda_{\text{Raman}} \left(\text{in A}^0 \right)} \\ &= \frac{10^8}{4358} - \frac{10^8}{4452} = 484.49 \text{ cm}^{-1} \end{aligned}$$

- (b) The anti stokes line will appear at a frequency 484.49 cm^{-1} higher than the frequency (cm^{-1}) associated with 4358 Å⁰. Hg line used as source of excitation hence

$$\Delta \bar{\nu}_{\text{exc}} \left(\text{in cm}^{-1} \right) = \frac{10^8}{\lambda_{\text{exc}} \left(\text{in A}^0 \right)} = \frac{10^8}{4358 \text{ A}^0} = 2.295 \times 10^4 \text{ cm}^{-1}$$

$$\text{hence } \bar{\nu}_{\text{antistokes}} = 2.295 \times 10^4 \text{ cm}^{-1} + 484.49 \text{ cm}^{-1} = 2.3434 \times 10^4 \text{ cm}^{-1}$$

$$\lambda \left(\text{in A}^0 \right) = \frac{10^8}{\bar{\nu} \left(\text{in cm}^{-1} \right)} = \frac{10^8}{2.3434 \times 10^4} = 4267.3 \text{ A}^0$$

2. A radiation of wave number 19865 cm^{-1} is incident on a sample of $^{14}\text{N}_2$. If the equilibrium bond length is 110 pm, find the wave number of the scattered Stokes radiation for the transition $J = 0 \rightarrow 2$.

Solution

For a homonuclear diatomic molecule the reduced mass

$$\mu = \frac{14.0067 \times 10^{-3}}{2 \times 6.02214 \times 10^{23}} = 1.16293 \times 10^{-26} \text{ kg}$$

moment of inertia $I = \mu r^2$

$$= 1.16293 \times 10^{-26} \times (110 \times 10^{-12})^2$$

$$= 1.41 \times 10^{-46} \text{ kg m}^2$$

Rotational constant

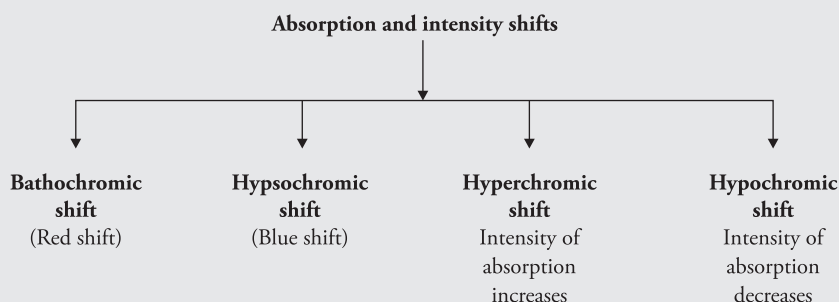
$$B = \frac{h}{8\pi^2 I c} = \frac{6.626 \times 10^{-34}}{8 \times (3.14)^2 \times 1.41 \times 10^{-46} \times 2.998 \times 10^{10}} = 1.985 \text{ cm}^{-1}$$

The Stokes line appears towards lower wave number side and for the transition $J = 0 \rightarrow 2$ it is at 6B. Therefore, the line will appear at $19865 - 6 \times 1.985 = 19853.09 \text{ cm}^{-1}$

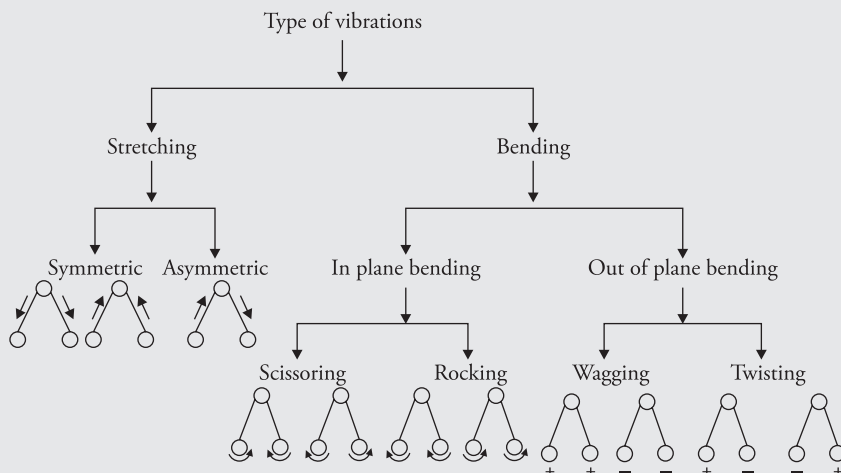
Summary

- Spectroscopy is the branch of science which deals with the interaction of electromagnetic radiation with matter. It is a very important tool for studying the structures of atoms and molecules.
- Electromagnetic spectrum is obtained when the electromagnetic radiations are arranged in the order of increasing wavelength or decreasing frequency.
- Electronic spectra are produced when electrons absorb energy and undergo change in their electronic, rotational or vibrational motions.
- Spectra can be continuous spectra, emission spectra or absorption spectra.
- The spectra of atoms is obtained as sharp lines which are characteristic of the atoms. Molecular spectra are obtained as bands.
- UV-visible spectroscopy is also called electronic spectroscopy and it involves the transition of (σ , π , n) electrons from the ground state to higher energy states.
- Ultraviolet spectroscopy is used to measure the number of conjugated double bonds, differentiate between conjugated and non-conjugated systems, detect geometrical isomers, hydrogen bonding, etc.
- Spectrometer or spectrophotometer is used to detect the spectra of compounds. It includes a light source (hydrogen/deuterium discharge lamp for UV-visible, Globar or Nernst glower for IR region), monochromator, sample holder (glass or quartz for UV-visible, NaCl, KBr for IR), detector and recorder unit.

- Franck Condon principle helps in interpreting the intensity distribution in an absorption spectrum.
- The various types of electronic transitions are
 $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$
- Chromophore is an isolated covalently bonded group that absorbs in the UV-visible region. Auxochrome does not act as a chromophore itself but shifts the absorption band towards the red end of the spectrum.



- Solvent effects
 - (i) Non-polar compounds (C_2H_4 , C_4H_6) No effect of solvent polarity
 - (ii) Polar compounds $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ Blue shift on increasing the solvent polarity.
 $\pi \rightarrow \pi^*$ Red shift on increasing solvent polarity
- Infrared spectroscopy occurs due to change in vibrational energy levels of bonds. A compound which undergoes net change in dipole moment on interaction with electromagnetic radiation is said to be IR active.
- Different types of vibrations are



- **Important IR absorption regions**

IR region extends from $4000\text{--}667\text{ cm}^{-1}$. It is studied under two regions.

(a) Functional group region ($4000\text{--}1500\text{ cm}^{-1}$)

(b) Finger print region ($1500\text{--}667\text{ cm}^{-1}$)

- Selection rule for vibration transition in a simple harmonic oscillator is $\Delta v = \pm 1$ and for anharmonic oscillator is $\Delta v = \pm 1, \pm 2, \pm 3$ and so on.

- **Important bands in IR region**

>C=O	$1900 - 1600\text{ cm}^{-1}$
$\text{—OH, —NH}_2, \text{>NH}$	$3600 - 3200\text{ cm}^{-1}$
$\equiv\text{C—H}$	3300 cm^{-1}
$=\text{C—H}$ and Ar—H	3200 cm^{-1}
—C—H	Just below 3000 cm^{-1}
$\text{C}\equiv\text{C}$	$2140 - 2100\text{ cm}^{-1}$
C—O (primary, secondary, tertiary alcohols, esters, ethers)	$1600 - 1000\text{ cm}^{-1}$
Aromatic compounds	Below 1000 cm^{-1}

- Nuclear magnetic resonance arises when nuclei of atoms/ molecules interact with electromagnetic radiations in the presence of an external magnetic field.
- In the presence of external magnetic field a spinning nucleus can be aligned with (α spin) or against (β spin) the field. There is energy difference in the two orientations. When radiated with a radiation of appropriate frequency, the nuclei absorb energy and change from α spin to β spin. This is called *flipping*.
- Nuclei with value of spin quantum number I greater than zero will be NMR active.
- The absorption of a nucleus with respect to TMS is called chemical shift.
- Chemical shift depends upon the neighbouring environment, shielding and deshielding effect of the nuclei.
- Anisotropic effects account for the unexpected absorptions of various nuclei in alkenes, alkynes, aromatic rings and carbonyl group protons.
- All protons in a similar environment are called equivalent protons and all equivalent protons give one signal in the NMR spectrum.
- Proton area gives information about the number of protons in each equivalent set present in the compound.
- The signals do not appear as singlets but as multiplets. The number of peaks in a multiplet is given by $n + 1$, where n is the number of neighbouring equivalent protons.
- UV, IR and NMR spectroscopy help in predicting the structures of compounds.

- The rotational spectra results from transitions between the rotational energy levels of a gaseous molecule on absorption of radiations falling in the microwave region.
- The selection rule for rotational transition (rigid rotor model) is $\Delta J = \pm 1$.
- The rotational frequency on transition from J to $J + 1$ is given by

$$\bar{\nu}_{J \rightarrow J+1} = 2B(J + 1) \text{ cm}^{-1} \quad (\text{rigid rotor})$$

$$\bar{\nu}_{J \rightarrow J+1} = 2(J + 1)\{B - 2D(J + 1)^2\} \quad (\text{non rigid rotor})$$
- Raman spectroscopy is based on the principle of scattering of incident light. If the frequency of incident and scattered light is the same it is called elastic *scattering or Rayleigh scattering*. If the frequency of scattered light is greater than or less than the frequency of incident light it is termed as *inelastic scattering or Raman scattering*.
- Classical theory explains Raman effect on the basis of polarisability of a molecule.
- Molecules like H_2 and N_2 , which are IR inactive, get polarised and become Raman active.
- If the frequency of scattered radiation is lower than that of incident radiation it is called Stokes radiation and if it is higher than it is called Antistokes radiation.
- Selection rule for vibrational Raman spectrum of a diatomic molecule is $\Delta v = \pm 1$.
- Selection rule for pure rotational Raman spectrum of a diatomic molecule is $\Delta J = 0, \pm 2$.

Review Questions

1. What is an electromagnetic radiation? Define the terms wavelength, frequency, velocity, wave number of a wave.
2. What is an electromagnetic spectrum? Give the regions of the electromagnetic spectrum in the order of increasing frequency. Differentiate between (i) absorption and emission spectra. (ii) atomic and molecular spectra.
3. What do you understand by the term spectroscopy? Explain different types of molecular spectra.
4. Why is UV-visible spectroscopy called electronic spectroscopy? What is the absorption range? Explain the Beer–Lambert’s law.
5. With the help of a neat, labelled diagram, explain the principle and working of a spectrophotometer. What is the difference between a single beam and a double beam spectrophotometer. Which of the two is better and why?
6. Explain in detail the various transitions taking place in UV-visible spectroscopy. Explain the effect of polarity of the solvent on each of these transitions
7. Explain the following
 - (i) Allowed and forbidden transitions
 - (ii) Chromophore
 - (iii) Auxochrome

8. Describe the various absorption bands which arise as a result of electronic transitions. Explain the effect of solvent polarity on K and R bands.
9. Explain the following with respect to UV-visible spectroscopy.
 - (i) Bathochromic or red shift
 - (ii) Hypsochromic or blue shift
 - (iii) Hypochromic shift
 - (iv) Hyperchromic shift
10. A conjugated diene absorbs at a higher wavelength with a higher value of extinction coefficient as compared to a diene in which the double bonds are isolated. Explain why.
11. Define infrared spectroscopy. Describe the various molecular vibrations responsible for IR absorption. Also explain the main requirement of a compound to be IR active.
12. Explain the following with respect to IR spectroscopy.
 - (i) Vibrational frequency
 - (ii) Dipole moment and infrared spectrum
 - (iii) Fundamental vibrations and overtones
 - (iv) Fermi resonance.
 - (v) Fingerprint region
13. Explain in detail the various factors affecting the vibrational frequency of the molecules.
14. How many vibrational modes are there in a linear and non-linear molecule having n atoms? Explain with the help of degrees of freedom.
15. Explain the theory of NMR spectroscopy. What kind of the nuclei exhibit NMR spectroscopy?
16. With the help of a well labelled diagram, explain the instrumentation in NMR spectroscopy.
17. What is meant by the term 'chemical shift'? Explain why tetramethylsilane is chosen as a reference for NMR spectroscopy.
18. What is shielding and deshielding? Explain giving suitable examples.
19. Define chemical shift. Describe the factors which influence chemical shift.
20. What do you understand by the term 'splitting of the signals'. Explain taking suitable examples.
21. Describe anisotropic effects in the following compounds.
 - (i) Alkenes
 - (ii) Alkynes
 - (iii) Benzene
 - (iv) Carbonyl compounds.
22. Explain why an aldehyde absorbs at a higher wave number than its corresponding methylketone due to their C = O vibrations.
23. In UV-spectroscopy explain why amines absorb at a higher wavelength in comparison to alcohols.
24. Explain the effect of hydrogen bonding in UV absorption.
25. What is Raman spectroscopy. How is it different from UV, IR and NMR spectroscopies. Explain in detail the classical theory of Raman effect.

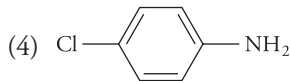
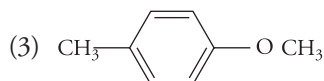
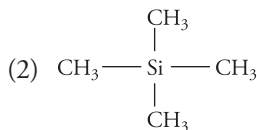
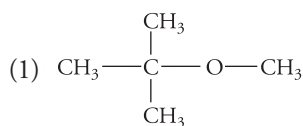
26. Explain the quantum theory of Raman scattering, prove that the energy difference between ground state and excited state $\Delta E_J = B(4J + 6) \text{ cm}^{-1}$. Also show how Stokes and Antistokes lines appear in the Raman spectrum of a molecule.
27. Explain the Franck – Condon principle. Using suitable potential energy curves illustrate the Franck Condon principle in the vibronic spectrum of a diatomic molecule.
28. Show that for a rigid diatomic rotor the moment of inertia is given by $I = \mu r^2$.
29. Using the energy level expression and selection rule draw an energy level diagram and spectral transitions for pure rotational (microwave) spectrum of a rigid diatomic rotor.

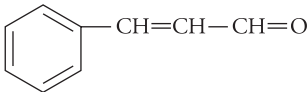
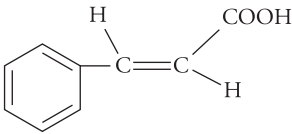
Multiple Choice Questions

1. The distance between the two adjacent crests or troughs of a wave is called its
 - (a) Wave length
 - (b) Frequency
 - (c) Wave number
 - (d) Velocity
2. The wave number of a radiation whose wavelength is 3.8μ is
 - (a) 2558.62 cm^{-1}
 - (b) 2631.57 cm^{-1}
 - (c) 2950.45 cm^{-1}
 - (d) 3000 cm^{-1}
3. Visible light lies between the wavelength range
 - (a) $3800\text{--}7600 \text{ \AA}$
 - (b) $2500\text{--}3800 \text{ \AA}$
 - (c) $3000\text{--}7000 \text{ \AA}$
 - (d) $7500\text{--}8000 \text{ \AA}$
4. The spectra of atoms and molecules are obtained as
 - (a) Sharp lines
 - (b) Bands
 - (c) Sharp lines and bands respectively
 - (d) Band and sharp line respectively
5. The light source in ultraviolet spectroscopy is
 - (a) Incandescent tungsten filament lamp
 - (b) Hydrogen and deuterium discharge lamp
 - (c) Nernst glower or Globar
 - (d) Klystron tube
6. Nernst glower or Globar is used as a light source in
 - (a) Visible spectroscopy
 - (b) Ultraviolet spectroscopy
 - (c) NMR spectroscopy
 - (d) Infrared spectroscopy
7. Glass cuvettes or samples holders are used in
 - (a) Visible spectroscopy
 - (b) Ultraviolet spectroscopy
 - (c) Infrared spectroscopy
 - (d) None of the above
8. Sample holders used in infrared spectroscopy are made up of
 - (a) Glass
 - (b) Quartz
 - (c) NaCl or KBr
 - (d) All the above

9. Detectors used in ultraviolet and infrared spectroscopy are
 - (a) Photocells and thermocouples, respectively
 - (b) Thermocouples and photocells, respectively
 - (c) Photocells for both
 - (d) Thermocouples for both
10. The relative energies required for various transitions are in the order
 - (a) $n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^* > \sigma \rightarrow \sigma^*$
 - (b) $\pi \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \rightarrow \pi^* > n \rightarrow \sigma^*$
 - (c) $\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \sigma^* > n \rightarrow \pi^*$
 - (d) $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$
11. K and R band arise due to the following transitions
 - (a) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively
 - (b) $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively
 - (c) $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ respectively
 - (d) $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ respectively
12. When the polarity of the solvent is decreased, the $n \rightarrow \pi^*$ transition of carbonyl compounds experiences
 - (a) Hyperchromic shift
 - (b) Hypochromic shift
 - (c) Bathochromic or red shift
 - (d) Hypsochromic or blue shift
13. On removal of conjugation, the spectra of a compound experiences
 - (a) Hypsochromic or blue shift
 - (b) Bathochromic or red shift
 - (c) There is no change in the position of absorption
 - (d) None of the above
14. Compound whose absorption maxima experiences very little shift on changing the polarity of the solvent are
 - (a) Carbonyl compounds
 - (b) Ethylene and butadiene
 - (c) Alcohols
 - (d) Amines
15. The most useful region of the IR spectrum for the purpose of study is
 - (a) 600 cm^{-1} to 50 cm^{-1}
 - (b) 12000 cm^{-1} to 8000 cm^{-1}
 - (c) 8000 cm^{-1} to 4625 cm^{-1}
 - (d) 4000 cm^{-1} to 667 cm^{-1}
16. The functional group region and fingerprint region of an IR spectra are respectively
 - (a) $4000\text{ cm}^{-1} - 1500\text{ cm}^{-1}$ and 1500 cm^{-1} to 667 cm^{-1}
 - (b) $4000\text{ cm}^{-1} - 2500\text{ cm}^{-1}$ and 2500 cm^{-1} to 1500 cm^{-1}
 - (c) 6000 cm^{-1} to 4500 cm^{-1} and 3500 cm^{-1} to 650 cm^{-1}
 - (d) 4500 cm^{-1} to 1800 cm^{-1} and 1800 cm^{-1} to 980 cm^{-1}
17. $\pi - \pi^*$ transitions will not be observed in the UV spectra of the following compounds.
 - (a) Alkenes
 - (b) Azo compounds
 - (c) Cyanides
 - (d) Alcohols

18. The theoretical number of vibrational degrees of freedom in benzene, carbon dioxide, sulphur dioxide and $C_6H_5-CH_3$, respectively, are
- (a) 39, 3, 4, 30 (b) 30, 3, 4, 39
(c) 30, 4, 3, 39 (d) 39, 4, 3, 30
19. Which of the following molecules will not show IR spectra?
- (a) H_2 (b) HCl
(c) SO_2 (d) H_2O
20. The characteristic absorption bands of carbonyl group in IR spectra are given below. Which one is incorrect?
- (a) $CH_3COCH_3 \sim 1765\text{ cm}^{-1}$ (b) $CH_3CHO \sim 1745\text{ cm}^{-1}$
(c) $C_6H_5CHO \sim 1700\text{ cm}^{-1}$ (d) $CH_3COOH \sim 1725\text{--}1700\text{ cm}^{-1}$
21. Match the following absorption frequencies
- | | | |
|----------------|-------------------|----------------------------------|
| (i) Alkanes | C-H str | (a) 3100 – 3000 cm^{-1} |
| (ii) Alkenes | $>C=C-H$ str | (b) 3050 – 3000 cm^{-1} |
| (iii) Alkynes | $C\equiv C-H$ str | (c) 2960 – 2850 cm^{-1} |
| (iv) Aromatics | Ar-H str | (d) $\sim 3300\text{ cm}^{-1}$ |
- (a) (i) a (ii) b (iii) c (iv) d
(b) (i) c (ii) a (iii) b (iv) d
(c) (i) b (ii) c (iii) d (iv) a
(d) (i) c (ii) a (iii) d (iv) b
22. The O-H str absorption for free OH group, intermolecular hydrogen bonded OH group and intramolecular hydrogen bonded OH group are, respectively
- (a) 3700 – 3500 cm^{-1} (sharp), 3400 – 3200 cm^{-1} (sharp), 3570 – 3450 cm^{-1} (broad)
(b) 3700 – 3500 cm^{-1} (sharp), 3400 – 3200 cm^{-1} (broad), 3570 – 3450 cm^{-1} (sharp)
(c) 3400 – 3200 cm^{-1} (broad), 3500 – 3400 cm^{-1} (broad), 3700 – 3500 cm^{-1} (sharp)
(d) 3700 – 3500 cm^{-1} (sharp), 3570 – 3450 cm^{-1} (sharp), 3400 – 3200 cm^{-1} (broad)
23. The number of NMR signals obtained from the following compounds will be, respectively



- (a) 1, 2, 3, 4 (b) 2, 3, 1, 2
(c) 2, 2, 3, 1 (d) 2, 1, 3, 2
24. How many different kinds of hydrogens are there in the following compounds, respectively
- (1) $\text{C}_6\text{H}_5\text{—CH}_3$ (2) $\text{CH}_3\text{—NH—C(=O)—O—CH}_2\text{—CH}_3$
- (3)  (4) 
- (a) 2, 3, 4, 2 (b) 2, 4, 4, 4
(c) 2, 4, 2, 3 (d) 2, 2, 2, 3
25. Which of the following compounds will exhibit NMR spectroscopy?
- (a) $^{12}_6\text{C}$ (b) $^{16}_8\text{O}$
(c) $^{13}_6\text{C}$ (d) $^{32}_{16}\text{S}$
26. Which of the following compounds will not exhibit NMR spectroscopy?
- (a) ^1_1H (b) $^{12}_6\text{C}$
(c) $^{13}_6\text{C}$ (d) $^{19}_9\text{F}$
27. The number of signals and multiplicity of the signals in $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ will be
- (a) 4 signals; singlet (2H), triplet (2H), triplet (3H), sextet (2H)
(b) 3 signals; singlet (2H), quartet (4H), quintet (3H)
(c) 4 signals; singlet (2H), triplet (2H), triplet (3H), quintet (2H)
(d) 2 signals; octet (2H), triplet (7H)
28. The chemical shift of a proton on δ scale is 6.5. The value on τ scale will be
- (a) 16.5 (b) 3.5
(c) 6.5 (d) 2.5
29. Pick the correct match
- | | |
|-------------------------------|----------------|
| (a) Pure rotational spectrum | Far infrared |
| (b) Pure vibrational spectrum | Microwave |
| (c) Electronic spectrum | Infrared |
| (d) NMR spectrum | Visible region |
30. The τ values of the methyl protons in methyl halides are in the order
- (a) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$ (b) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
(c) $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$ (d) $\text{CH}_3\text{I} < \text{CH}_3\text{Br} < \text{CH}_3\text{F} < \text{CH}_3\text{Cl}$

31. What is the correct order of different types of energies
- (a) $E_{\text{vib}} \gg E_{\text{el}} \gg E_{\text{trans}} \gg E_{\text{rot}}$. (b) $E_{\text{trans}} \gg E_{\text{el}} \gg E_{\text{vib}} \gg E_{\text{rot}}$
 (c) $E_{\text{el}} \gg E_{\text{vib}} \gg E_{\text{rot}} \gg E_{\text{trans}}$ (d) $E_{\text{el}} \gg E_{\text{rot}} \gg E_{\text{vib}} \gg E_{\text{trans}}$
32. The centre of gravity of a molecule changes in
- (a) Translational motion (b) Rotational motion
 (c) Vibrational motion (d) Electronic motion
33. The equilibrium bond length of $^1\text{H}^{35}\text{Cl}$ molecule is 1.275 \AA . Calculate its moment of inertia if masses of the two atoms are $m_{\text{H}} = 1.673 \times 10^{-27} \text{ kg}$ and $m_{\text{Cl}} = 5.807 \times 10^{-26} \text{ kg}$.
- (a) $2.644 \times 10^{-26} \text{ kg m}^2$ (b) $2.644 \times 10^{-47} \text{ kg m}^2$
 (c) $2.644 \times 10^{47} \text{ kg m}^2$ (d) $2.644 \times 10^{26} \text{ kg m}^2$
34. Calculate the rotational constant of a molecule if the first Stokes line and first Antistokes line in its rotational spectrum are displaced from the Rayleigh line by 2.842 cm^{-1} and $+ 2.842 \text{ cm}^{-1}$ respectively
- (a) 0.4951 cm^{-1} (b) 0.4736 cm^{-1}
 (c) 0.8360 cm^{-1} (d) 1.459 cm^{-1}
35. Which of the following molecules is IR active but Raman inactive
- (a) Benzene (b) NO_2
 (c) Chlorobenzene (d) Nitrobenzene
36. Which of the following transitions between rotational energy levels is not allowed
- (a) $J = 0 \leftarrow J = 1$ (b) $J = 1 \leftarrow J = 2$
 (c) $J = 1 \rightarrow J = 0$ (d) $J = 1 \leftarrow J = 3$

Solutions

1. (a) 2. (b) 3. (a) 4. (c) 5. (b) 6. (d) 7. (a) 8. (c) 9. (a) 10. (d)
 11. (b) 12. (c) 13. (a) 14. (b) 15. (d) 16. (a) 17. (d) 18. (c) 19. (a) 20. (a)
 21. (d) 22. (b) 23. (d) 24. (b) 25. (c) 26. (b) 27. (a) 28. (b) 29. (a) 30. (c)
 31. (c) 32. (a) 33. (b) 34. (b) 35. (a) 36. (d)

Chapter 18

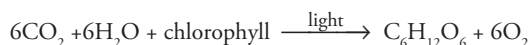
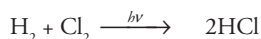
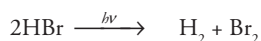
PHOTOCHEMISTRY

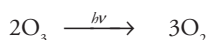
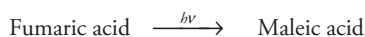
18.1 Introduction

Generally speaking, all chemical reactions require energy over and above the average kinetic energy of the molecules. The reactant molecules convert into products only after acquiring this extra energy called the activation energy. Sometimes, this activation energy is very low and the molecules can undergo spontaneous transformations even at room temperatures. However, in most cases, additional energy has to be supplied to the molecules to bring about the chemical change. If this extra energy is provided by absorption of heat from outside, then the reactions are called thermal or thermochemical reactions. In thermal reactions, the provided heat is distributed among the molecules such that all the molecules in the system have almost the same energy. When they acquire sufficient energy, they react to form products. Another way of providing activation energy to the molecules is by the absorption of electromagnetic radiation in the visible and ultraviolet region. Such reactions are termed as photochemical reactions. Unlike thermal conditions, in photochemical reactions, the absorption of light excites an individual molecule to an excited electronic state without affecting the surrounding molecules (Table 18.1). This selective excitation of individual molecules is a unique character of photochemical reactions. The chemistry of the excited state is different from that of the ground state. The reaction occurs and the molecule gradually returns to its ground state.

The radiations can range from radiowaves to γ -rays, but for all practical purposes, the light radiations of visible and ultraviolet regions lying between 2000 and 8000 Å are considered, because these radiations possess sufficient energy to excite molecules from the ground state to higher electronic states.

Common examples of photochemical reactions are given below.





Photochemistry is defined as the study of chemical effects produced by light radiations ranging from 2000 to 8000 Å wavelength.

Table 18.1 Difference between thermal and photochemical reactions

Photochemical reaction	Thermochemical reaction
In photochemical reactions, the activation energy is acquired by the absorption of light radiations (visible or ultraviolet).	In thermochemical reactions, the activation energy is provided by collisions.
These reactions occur only in the presence of light.	These reactions can occur both in the presence or absence of light radiations. Since they can occur in the absence of light, they are also called dark reactions.
These reactions involve the absorption of light radiation.	These reactions involve both absorption (endothermic) and evolution of heat (exothermic).
Photochemical reactions can occur spontaneously both by the increase or decrease of free energy, hence ΔG can be either positive or negative. Photochemical reactions like photosynthesis in plants, ozonisation of oxygen, polymerisation of anthracene are accompanied by an increase in free energy, i.e., ΔG for these reactions is positive.	Thermal reactions, whether endothermic or exothermic, proceed invariably by the decrease in free energy, i.e., ΔG for thermal reactions is always negative.
Temperature does not have a marked effect on the rate of a photochemical reaction. In fact, the rate of reaction is affected by the intensity of the incident radiations.	The rate of a thermal reaction is affected significantly by the variation in temperature. The reaction rate normally increases with the rise in temperature.
In photochemical reactions, individual molecules are prompted to the excited state by the absorption of incident radiation of a specific wavelength. The neighbouring molecules are not affected. Hence photochemical excitations are highly selective. For example, when a mixture of H_2 and Br_2 is exposed to a radiation of wavelength between 450 nm and 550 nm, only Br_2 molecules are excited.	In thermal reactions, rise in temperature increases the average energy of all molecules in the system. Hence, thermochemical excitations are not specific. For example, when a mixture of H_2 and Br_2 is heated, both hydrogen and bromine molecules will be excited.

18.2 Significance of Photochemistry

Photochemistry finds applications in varied fields. It helps to save energy and enables the sustainable use of resources. Since solar energy is abundantly available and photochemical reactions are selective, they can help to carry out reactions under mild conditions, thus saving energy. Photochemistry finds use in the production of solar cells (photovoltaic cells), in catalysis and in pollution control. Photosynthesis and vision are some common examples of photochemical reactions involving

supramolecules (explained later in this chapter). Supramolecular photochemistry finds use in micelles, production of optical sensors and devices like molecular machines, switches, molecular wires, light harvesting antennas, etc.

18.3 Laws Governing Light Absorption

Beer lambert's law: Please refer to chapter on spectroscopy, Section 15.2.

18.4 Laws of Photochemistry

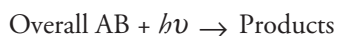
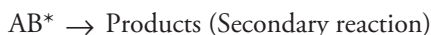
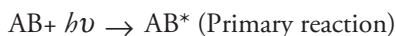
Photochemical reactions are governed by two basic laws.

1. **Grotthuss–Draper law** This law given by Grotthuss in 1881 and reaffirmed by Draper in 1841 is termed as the first law of photochemistry and states that when light is incident on any substance, only that portion of the incident light which is absorbed by the substance brings about the chemical reaction. The reflected and transmitted light has no role in the reaction. It may be noted here that it is not necessary that all the absorbed radiations be effective in bringing about the desired chemical change. When the conditions are not favourable, the absorbed light may be converted to heat or may be re-emitted as radiations of the same or another frequency.

Grotthuss–Draper law is a purely qualitative law and gives no relationship between the amount of light absorbed and the number of molecules reacted.

2. **Stark–Einstein law of photochemical equivalence** According to quantum theory of light, energy is emitted or absorbed in small packets of quanta. Stark and Einstein (1905) applied the quantum theory of light to the photochemical reactions and enunciated the law of photochemical equivalence also termed as the second law of photochemistry. It states that *each molecule taking part in the chemical reaction absorbs one quantum of light and on absorbing one photon equivalent energy, it gets excited and induces the reaction.*

The term 'one photon' or 'one quantum' means energy equal to $h\nu$, where h is the Planck's constant and ν is the frequency of radiation.



A photochemical reaction may consist of a primary and secondary reaction. The primary reaction proceeds by the absorption of radiation and strictly obeys the law of photochemical equivalence, that is, a molecule (say AB) gets excited (AB^*) by absorbing a quanta of energy. The second step or the secondary reaction occurs subsequent to the primary reaction. It is a thermal reaction that does not follow the law of photochemical equivalence. In this step, the excited molecule (AB^*) decomposes to form the products.

Thus, it is only in the primary process that the number of molecules that are activated is equal to the quanta absorbed.

$$\text{Energy per quantum} = h\nu = \frac{hc}{\lambda}$$

Thus the energy of a photon is proportional to its frequency and is inversely proportional to its wavelength. The energy of the photon is measured in J or kJ. The mole of photons (6.02×10^{23} photons) is called an einstein and is measured in kJ mol^{-1} . Energy of one einstein of light of wavelength λ is given by

$$\text{Energy per einstein} = N h \nu = N h \frac{c}{\lambda}$$

where N = Avogadro's number
Substituting the values,

$$N = 6.023 \times 10^{23} \text{ molecules} \quad h = 6.624 \times 10^{-34} \text{ J s}$$

$$c = 3 \times 10^8 \text{ m s}^{-1}$$

$$E = \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-34} \times 3 \times 10^8}{\lambda(\text{m})} = \frac{0.1196}{\lambda(\text{m})} \text{ J mol}^{-1} \text{ in SI units}$$

$$= \frac{0.1196}{\lambda} \times 10^{10} \text{ J (when } \lambda \text{ is in } \text{\AA} \quad \because 1 \text{\AA} = 10^{-10} \text{ m)}$$

Sometimes energy is measured in electronvolts (eV), where $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$

In CGS units,

$$c = 3 \times 10^{10} \text{ cm s}^{-1}, \quad h = 6.624 \times 10^{-27} \text{ erg s}^{-1}$$

$$E = \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-27} \times 3 \times 10^{10}}{\lambda} \text{ erg mol}^{-1}$$

$$= \frac{1.196 \times 10^8}{\lambda(\text{in cm})} \text{ erg mol}^{-1} = \frac{1.196 \times 10^{16}}{\lambda(\text{in } \text{\AA})} \text{ erg mol}^{-1}$$

since $1 \text{ cal} = 4.184 \times 10^7 \text{ ergs}$

$$\begin{aligned} \therefore E &= \frac{1.196 \times 10^{16}}{4.184 \times 10^7 \lambda (\text{in } \text{\AA})} \text{ cal mol}^{-1} \\ &= \frac{2.859 \times 10^8}{\lambda(\text{in } \text{\AA})} \text{ cal mol}^{-1} \\ &= \frac{2.859 \times 10^5}{\lambda(\text{in } \text{\AA})} \text{ kcal mol}^{-1} \end{aligned}$$

It is evident from the above relations that

$$E \propto \frac{1}{\lambda}$$

Hence, shorter the wavelength, greater will be the energy. For a wavelength of 4000 Å (ultraviolet light), the energy is 71 kcal and the energy associated with wavelength of 7500 Å (red light) is 38 kcal. Hence, in ultraviolet light, the violet portion of radiation having more energy will be more active in bringing about photochemical reactions.

18.5 Quantum Yield or Quantum Efficiency

Quantum yield is defined as the number of molecules reacted or formed per photon of light absorbed. It is denoted by Φ . (Remember that primary quantum yield is denoted by the symbol ϕ and the overall quantum yield is denoted by Φ).

$$\text{Quantum yield } (\Phi) = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of photons absorbed in the same time}}$$

$$\text{or } \Phi = \frac{\text{Number of moles reacting in a given time}}{\text{Number of einsteins absorbed in the same time}}$$

According to the law of photochemical equivalence, one molecule reacts or decomposes per photon of light absorbed. Hence ideally, the quantum efficiency for all photochemical reactions should be one. Yet, quantum efficiency is seldom unity. It is generally either greater than one or less than unity. If the number of molecules reacting or formed per photon of light absorbed is more than one, then $\Phi > 1$ and the reaction has a high quantum yield (Table 18.2). If the number of molecules decomposed or formed per photon of light absorbed is less than one, $\Phi < 1$ and the reaction has low quantum yield.

Table 18.2 Quantum yield

S.No	Reaction	Quantum Yield
1.	Reactions with quantum yield one ($\Phi = 1$)	
(i)	$2\text{Fe}^{3+} + \text{I}_2 \xrightarrow{5790 \text{ Å}} 2\text{Fe}^{2+} + 2\text{I}^-$ <p>This reaction is carried out in the liquid phase</p>	$\Phi = 1$
(ii)	$\text{SO}_2 + \text{Cl}_2 \xrightarrow{4200 \text{ Å}} \text{SO}_2\text{Cl}_2$	$\Phi = 1$
2.	Reactions with high quantum yield ($\Phi > 1$)	
(i)	$2\text{HBr} \xrightarrow{2070-2530 \text{ Å}} \text{H}_2 + \text{Br}_2$	$\Phi = 2$
(ii)	$\text{CO} + \text{Cl}_2 \xrightarrow{4000-4360 \text{ Å}} \text{COCl}_2$	$\Phi = 10^3$
(iii)	$\text{H}_2 + \text{Cl}_2 \xrightarrow{<4500 \text{ Å}} 2\text{HCl}$	$10^4 \text{ to } 10^6$

(iii)	$2\text{H}_2\text{O}_2 \xrightarrow{\sim 3100 \text{ Å}} 2\text{H}_2\text{O} + \text{O}_2$	More than 7
(iv)	$3\text{O}_2 \xrightarrow{1700-1900 \text{ Å}} 2\text{O}_3$	3
(v)	$2\text{HI} \xrightarrow{2070-2823 \text{ Å}} \text{H}_2 + \text{I}_2$	2
3	Reactions with low quantum yield, $\Phi < 1$	
(i)	$\text{H}_2 + \text{Br}_2 \xrightarrow{5100 \text{ Å}} 2\text{HBr}$	0.01
(ii)	$2\text{NH}_3 \xrightarrow{2100 \text{ Å}} \text{N}_2 + 3\text{H}_2$	0.2
(iii)	$\text{CH}_3\text{COCH}_3 \xrightarrow{3000 \text{ Å}} \text{CO} + \text{C}_2\text{H}_6$	0.1
(iv)	$\begin{array}{ccc} \text{H}-\text{C}-\text{COOH} & \xrightarrow{2000-1800 \text{ Å}} & \text{H}-\text{C}-\text{COOH} \\ & & \\ \text{H}-\text{C}-\text{COOH} & & \text{HOOC}-\text{C}-\text{H} \\ \text{Maleic acid} & & \text{Fumaric acid} \end{array}$	0.04
(v)	$2\text{C}_{14}\text{H}_{10} \xrightarrow{3600 \text{ Å}} \text{C}_{28}\text{H}_{20}$	0.25

Reasons for high and low quantum yields

As discussed earlier (Section 18.4), a photochemical reaction proceeds in two steps. The first step which absorbs the quanta of light and activates the molecules is called the primary process; in the second step, called the secondary process, these activated molecules undergo further reaction, forming the products. Light is not absorbed in the second step and it can also proceed in the dark. Hence, the quantum yield depends upon the number of quanta absorbed in the primary process and the number of molecules undergoing the reaction in the secondary process. Now we will discuss the reasons for different quantum yields of different reactions on the basis of the secondary process.

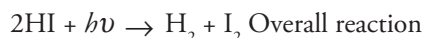
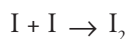
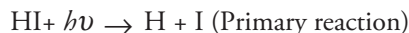
(i) Reasons for high quantum yield

- When free radicals are formed in the primary process of light absorption, these free radicals initiate a secondary chain reaction resulting in the formation or decomposition of large number of molecules. Hence the quantum yield is very high.
- One photon absorbed in the primary step dissociates one molecule of the reactant. A subsequent secondary reaction may be started by this excited atom which further decomposes molecules.

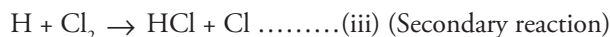
Common examples are given below.

- (a) **Decomposition of HI** It occurs by the absorption of light of wavelength less than 4000 Å . In the primary process, a molecule of hydrogen iodide absorbs a photon and dissociates into H and I. In the secondary process, H produced in the first step (primary process) further reacts with another HI molecule. In the overall reaction, two molecules

of HI are decomposed by the absorption of one photon of light. Thus, the quantum yield is 2. The reaction is represented as follows.



- (b) **Combination of hydrogen and chlorine** The quantum yield of this reaction is very high (of the order of 10^4 to 10^6). This is because in the primary process, a molecule of chlorine absorbs a photon and dissociates into two Cl atoms. The Cl atoms initiate a chain reaction in the secondary process.

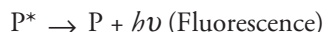


The Cl atom used in step (ii) is regenerated in step (iii). Hence, a self propagating chain reaction is initiated, producing two molecules of HCl in each cycle. Thus, one photon absorbed in step (i) leads to the formation of many HCl molecules by the repetition of steps (ii) and (iii). A large number of HCl molecules are formed by the absorption of a single photon. Therefore, the quantum yield is very high. The reaction terminates by the combination of Cl atom at the walls of the vessel where they lose their excess energy.

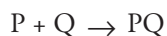
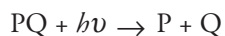
(ii) Reasons for low quantum yield

The main reasons for low quantum yield are as follows.

- The activated molecules formed in the primary process may get deactivated either by the collision with an inert molecule or due to loss of energy by fluorescence.

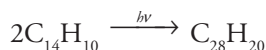


- The primary photochemical reaction may get reversed.
- The fragment formed in the primary process may recombine

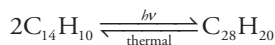


Some examples of low quantum yield are given below.

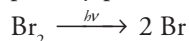
- (a) **Dimerisation of anthracene** Anthracene dissolved in benzene when exposed to light dimerises to give dianthracene, $\text{C}_{28}\text{H}_{20}$.



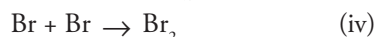
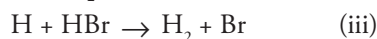
The quantum yield should be 2 but in reality, it is only 0.2. The quantum yield of the reaction is low because the reaction involves a reverse thermal reaction till equilibrium is reached. The reaction is also accompanied by fluorescence which deactivates the activated anthracene.



- (b) **Combination of H_2 and Br_2** The quantum yield of this reaction is only 0.01. The primary process involves the dissociation of bromine molecule into bromine atoms.



The expected secondary processes are



Since reaction (i) is highly endothermic, it takes place very slowly at room temperature. Thus, reactions (ii), (iii) and (iv) cannot occur, since they can proceed only after the completion of step (i). Under such conditions, the bromine atoms recombine to form bromine molecule.

Solved Examples

1. Calculate the energy associated with (a) one photon and (b) one einstein of radiation of wavelength 7500 Å.

$$h = 6.62 \times 10^{-27} \text{ erg-s}; \quad \text{velocity of light } c = 3 \times 10^{10} \text{ cm s}^{-1}$$

Solution

$$\text{(a) Energy of photon} = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{7500 \times 10^{-8}} = 2.648 \times 10^{-12} \text{ erg}$$

$$\begin{aligned} \text{(b) Energy per einstein} &= \frac{Nhc}{\lambda} \\ &= \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-27} \times 3 \times 10^{10}}{7500 \times 10^{-8}} = 1.5958 \times 10^{12} \text{ erg} \end{aligned}$$

2. 0.002 moles of a substance X reacted in 18 min and 5 s. The number of photons absorbed per second is 2.0×10^6 . Calculate the quantum yield of the reaction (Avogadro's number = 6.02×10^{23}).

Solution

Number of molecules of X reacting = 0.002 moles

$$= 0.002 \times 6.02 \times 10^{23}$$

Number of photons absorbed per second = 2.0×10^6

Number of photons absorbed in 18 min and 5 s = $2.0 \times 10^6 \times 1085$

$$\text{Quantum yield} = \frac{\text{Number of molecules reacted}}{\text{Number of photons absorbed}}$$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{2.0 \times 10^6 \times 1085} = 5.548 \times 10^{11}$$

3. 1×10^{-4} mole of a substance decomposed when it was irradiated with a light of wavelength 4800 Å. If the quantum efficiency of the reaction is 8, calculate the number of photons absorbed (Avogadro's number = 6.02×10^{23}).

Solution

Quantum efficiency of the reaction = 8

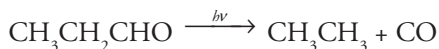
Number of moles decomposed = 1×10^{-4}

Number of molecules decomposed = $1 \times 10^{-4} \times 6.023 \times 10^{23} = 6.023 \times 10^{19}$

Quantum yield $\Phi = \frac{\text{Number of molecules decomposed}}{\text{Number of photons absorbed}}$

$$\therefore \text{Number of photons absorbed} = \frac{6.023 \times 10^{19}}{\text{Quantum yield } \Phi} = \frac{6.023 \times 10^{19}}{8} = 7.528 \times 10^{18}$$

4. Propionaldehyde decomposes to form carbon monoxide when irradiated with a light of wavelength 3020 Å.



The quantum yield for the reaction is 0.54. If 14050 erg mol of light is absorbed in a given time, find the number of moles of carbon monoxide formed in the same time.

Solution

We know that

$$\text{one einstein (E)} = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}$$

when $\lambda = 3020 \text{ Å}$

$$\text{One einstein} = \frac{1.196 \times 10^{16}}{3020} \text{ erg mol}$$

$$\text{or } 14050 \text{ erg mol of energy} = \frac{14050 \times 3020}{1.196 \times 10^{16}} = 3.547 \times 10^{-9} \text{ einstein}$$

$$\Phi = \frac{\text{No. of moles of CO formed}}{\text{No. of einstein absorbed}} = 0.54$$

$$\begin{aligned} \text{Hence moles of CO formed} &= 0.54 \times 3.547 \times 10^{-9} \\ &= 1.915 \times 10^{-9} \text{ mol} \end{aligned}$$

Practice problems

1. In the photochemical reaction



1.0×10^{-5} moles of A are formed on absorption of 6.62×10^7 ergs at 3600 \AA . Calculate the quantum yield. [Ans 0.5016]

2. Photobromination of cinnamic acid to dibromocinnamic acid was carried out in a light of wavelength 440 nm . Using light intensity of $1.5 \times 10^{-3} \text{ J s}^{-1}$, an exposure of 20 minutes decrease 0.075 m mol of Br_2 . The solution absorbed 80% of the light passing through it. Calculate the quantum yield of the reaction. [Ans 14.15]

18.6 Electronic Excitation

We know that an orbital can accommodate a maximum of two electrons and that during bond formation two atomic orbitals combine to form two molecular orbitals – one of which has lower energy and is referred to as the bonding molecular orbital and the other has higher energy and is termed as the anti-bonding molecular orbital. When the anti-bonding molecular orbital remains vacant, it is the ground state. On absorbing light energy, the bonding molecular orbitals are excited to the anti-bonding molecular orbitals. Four types of electronic transitions occur.

$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$. (For details on different types of electronic transition refer to the chapter on spectroscopy.)

18.7 Jablonski Diagram

The phenomenon of electronic transition associated with the absorption of light is well illustrated with the help of the Jablonski diagram.

The electrons are paired in the ground state with anti-parallel spins. On absorbing the correct amount of energy, the electrons from the ground state designated as S_0 are excited without spin inversion so that the electrons remain paired in the excited state. This is called the excited singlet state designated as S_1 , S_2 or S_3 . Depending upon the energy of the photon, the electron can be excited to S_1 or S_2 or S_3 state (S_2 and S_3 represent the higher vibrational level of the upper excited state). This electronic excitation is followed by spin inversion giving rise to a new excited state called the triplet state designated as T_1 , T_2 or T_3 . For each excited singlet state (S_1 , S_2 , S_3), there is a corresponding triplet state (T_1 , T_2 , T_3). The various electronic excited states are shown in Figure 18.1.

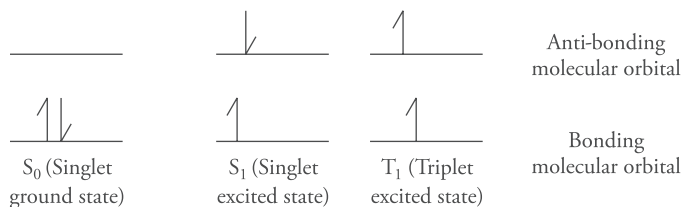


Figure 18.1 Various electronic excited states

The singlet states do not split in a magnetic field whereas the triplet state splits as it has three possible energy states in an applied magnetic field.

The direct excitation of the ground state (S_0) to a triplet state is not possible. Hence, a triplet state is invariably populated via the singlet state. According to the selection rules, direct transition from ground state (S_0) to a triplet state (T_1) is a forbidden transition. The terms 'singlet' and 'triplet' owe their origin to the fact that the singlet state does not split in a magnetic field whereas the triplet states have three possible energy states in an applied magnetic field.

The energy of a singlet state is higher than that of the triplet state; hence, a triplet state is more stable than a singlet state. Moreover, in triplet state, the spin of electrons is parallel and hence there is lesser inter-electronic repulsion than with the paired electrons in the singlet state.

Let us now see what happens after the electronic transition to the higher electronic states, S_2 and S_3 . The life time of the upper excited singlet state is less than 10^{-11} s and the electrons decay to the lower level S_1 by a process called internal conversion. Of all the excited singlet states, the vibrational level S_1 has the longest life of 10^{-8} s and is very important in photochemistry. The S_1 state may undergo the following energy degrading process.

- It may return to the ground level S_0 by a non-radiative process and the excess energy is shuffled between the various vibrational modes.
- It may drop to the ground level S_0 by emitting energy as a photon. This process is called fluorescence and occurs within 10^{-9} to 10^{-6} seconds.
- It may undergo photochemical reactions in the excited singlet state.
- Most of the molecules in the S_1 states drop to triplet state T_1 . The transition from $S_1 \rightarrow T_1$ occurs by a non-radiative process called the intersystem crossing (ISC). Since direct transition from S_0 to T_1 is forbidden, the triplet states are populated via ISC. A triplet state is populated via ISC and has a longer life (10^{-3} to 1 s) than the corresponding singlet state. The electrons in the triplet state either undergo chemical reaction or return to the ground state by dissipating energy through a process called phosphorescence. It can also undergo radiation-less decay to the ground state.

This process is presented in the Jablonski diagram shown in Figure 18.2.

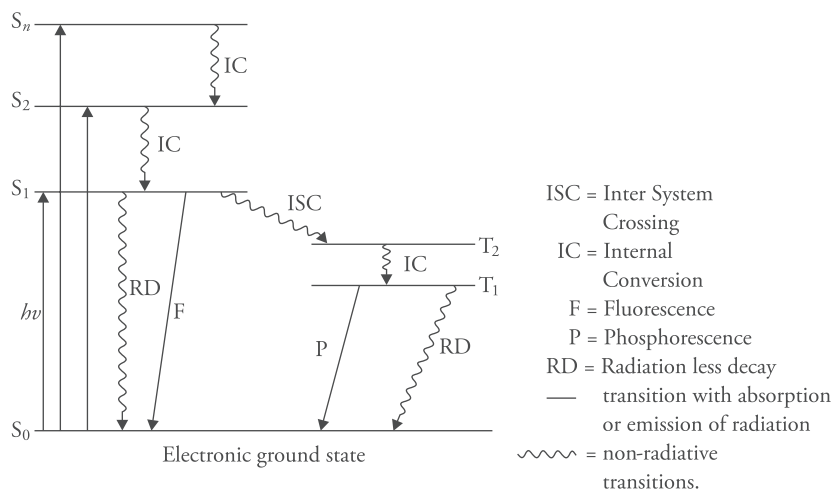


Figure 18.2 Jablonski diagram

18.8 Photophysical Processes

As discussed in the previous section, the electrons in the excited singlet or triplet state either undergo chemical reaction or return to the ground state by emitting radiations of longer wavelengths. Fluorescence and phosphorescence collectively known as luminescence are two such photophysical processes which occur commonly.

1. **Fluorescence** Certain substances emit long wavelength radiations under the influence of a beam of light. The radiations are emitted only as long as light is incident on them. As soon as incident light is cut off, they stop emitting radiations. This process is called fluorescence and the substance exhibiting this phenomenon is called a fluorescent substance.

Fluorescence occurs when a substance in the ground state is excited to the singlet state. When this returns to ground state, it emits long wavelength radiations and the phenomenon is termed as fluorescence. Fluorescence is generally stimulated by light of the visible and ultraviolet region of the spectrum. Different substances exhibit fluorescence with light of different wavelengths. For example, fluorspar fluoresces with blue light, a solution of chlorophyll in ether with red light, uranium glass with green light.

Applications

The phenomenon of fluorescence is a well-established analytical tool and is widely used in the medical field and in industry. Some common applications are as follows:

- **Food stuffs** The quality of food stuffs can be ensured by fluorescence. When ultraviolet light is incident on eggs, fresh eggs fluoresce with a rosy colour, while stale eggs appear blue. Similarly, butter, honey and various other food stuffs can be examined for their freshness and quality.
- **Medical field** When fluorescent liquids are injected into the body, the internal organs fluoresces and can be observed under special type of fluorescent microscopes. This helps

the doctors to detect disease without any difficulty. Ringworms can be detected by fluorescence caused by ultraviolet radiations.

- **Analytical method** Fluorescent indicators like eosin, fluorescein, quinine sulphate and acridine are used in acid–base titrations of coloured solutions. The colour and intensity depends upon the pH of the solution.
- (i) Calcium can be estimated by fluorimetry with calcein solution.
- (ii) Vitamin B₁ (thiamine) is non-fluorescent but its oxidation product thiochrome fluoresces with blue colour. This property helps in the determination of vitamin B₁ in food samples like cereals, meat, etc.
- (iii) It helps to detect aromatic compounds in smoke, automobile exhausts, etc.
- (iv) It is used in the analysis of drugs and dyes, textile and paper, fuels, chemicals, etc.
- (v) Fluorescence also finds use in the determination of cracks in metals and also in tracing the course of rivers through caves.
- **Lamps** Ultraviolet light produced by mercury arc lamps is used in tubes coated on the inside with fluorescent substances.
- **Science** It helps in seeing invisible radiations like ultraviolet radiations. The difference in fluorescence caused by ultraviolet rays in different types of inks helps police detect forged documents, forged signatures and so on.
- **Fluorescent paints** Fluorescent dyes are mixed with paints to produce extra brightness and lustre. These paints are used in advertisement hoardings.

2. Phosphorescence

It is a type of delayed fluorescence in which light is emitted continuously by the substance even after the incident light is cut off. Substances exhibiting this phenomenon are phosphorescent substances.

Phosphorescence occurs when an electron in the excited triplet state returns to the ground state with the emission of radiation. Since it occurs from the triplet state, it is long lived. Its longest lifetime is around 30 s (whereas the longest lifetime of fluorescence is around 10^{-6} s). Phosphorescence is caused by the ultraviolet and violet parts of the spectrum and is shown mainly by solids because in solids the molecules get sufficient time for crossing from the S₁ to the T₁ state.

Minerals like ruby and emerald are phosphorescent substances. Besides these, sulphates of calcium, barium and strontium exhibit phosphorescence. Many dyes show fluorescence in ordinary light in aqueous solution but when dissolved in fused boric acid or glycerol, they exhibit phosphorescence; for example, fluorescein in boric acid shows phosphorescence in the blue region at 5700 Å wavelength.

Applications of phosphorescence

Like fluorescence, phosphorescence also finds applications in the field of biology, medicine and in analytical analysis. The technique is called phosphorimetry and in combination with various extraction procedures, it finds use in the determination of low concentrations of procaine and cocaine in blood serum and urine. Although more sensitive than fluorimetry, phosphorimetry has limited applications because it is more complicated.

Chemiluminescence

Some chemical reactions are accompanied by the emission of visible light. This phenomenon of emission of visible light as a result of a chemical change is called chemiluminescence. It is the reverse of a photochemical reaction in which absorption of light causes chemical reaction. The light emitted due to chemiluminescence is also called 'cold light' because it is produced at ordinary temperature.

The phenomenon of chemiluminescence is explained on the basis of quantum theory. It is believed that the energy released in the chemical reactions makes the product electronically excited. When the excited product returns to ground level, the extra energy is emitted in the form of visible light. Common examples of chemiluminescence are given below.

- Phosphorus which produces a greenish-yellow glow. It is assumed that the phosphorus vapours get oxidised with atmospheric oxygen forming phosphorus trioxide which produces the glow.
- 5-aminophthalic cyclic hydrazide (luminol) gets oxidised by hydrogen peroxide in alkaline solution producing bright green light.

Bioluminescence

Certain living organisms exhibit the phenomenon of chemiluminescence and emit light. This is called bioluminescence. Common examples are given below.

- Fire fly or glow worm (*jugnu*) emits cold light due to the aerial oxidation of a protein luciferon in the presence of enzyme luciferase.
- Many marine fish emit powerful light. The protozoa *Noctiluca* of the sea also produces bioluminescence.

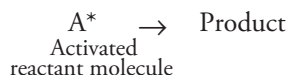
18.9 Photosensitisation

Some reactants are not sensitive to light and they do not absorb the radiation required for the reaction. If a photosensitive foreign substance is added to such reactants, then this foreign substance absorbs light and stimulates the reaction without itself participating in the reaction. This foreign substance is the photosensitiser and the phenomenon is called photosensitisation.

The photosensitiser absorbs the incident radiation and gets excited. This excited molecule collides with the reactant molecules and transfers the excitation energy to it, thereby activating the reactant molecules and returning to the original unactivated state. The activated reactant now undergoes reaction forming the product.

If P is the photosensitiser and A are the reactant molecules, then

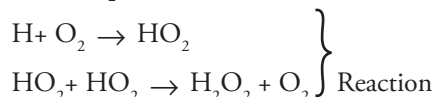
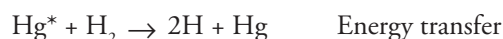




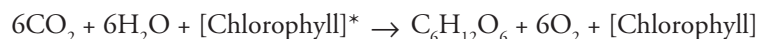
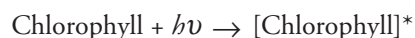
The photosensitiser thus acts as an energy carrier. Earlier, the process was considered akin to catalysis, but later, it was proved that photosensitisation is very different from ordinary catalysis.

Some common examples are given below.

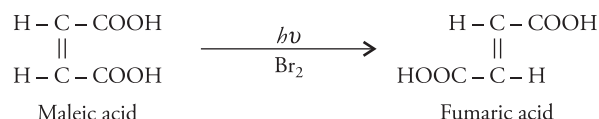
1. The reaction between H_2 and O_2 forming H_2O_2 is photosensitised by mercury vapours.



2. Chlorophyll acts as a photosensitiser in the formation of carbohydrates from CO_2 and H_2O .



3. Bromine acts as a photosensitiser in the conversion of maleic acid to fumaric acid.



18.10 Semiconductor Photochemistry

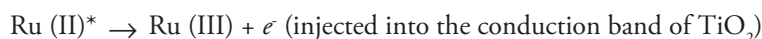
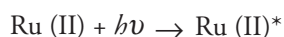
As discussed in Section 10.13, solids consist of three energy bands – the valence band, forbidden band and the conduction band. In semiconductors, the electrons occupy the valence band and the conduction bands are vacant. The forbidden energy band separating the valence and conduction band is very small (0.7 eV in germanium and 1.1 eV in silicon). When a semiconductor like TiO_2 , ZnO , SrTiO_3 , CdS and ZnS is irradiated with photon of energy equal to this forbidden energy band, the electrons are promoted from the valence band to the conduction band creating holes in the valence band and free electrons in the conduction band. These electrons and holes are used for various applications.

- (i) Photovoltaic cells** These are cells which convert light energy into electric energy. Photovoltaic cells are generally made by doping silicon with either an electron rich element like arsenic or phosphorus providing an extra electron to silicon or an electron deficient element like gallium or indium. The former results in an n-type semiconductor in which the extra electron can easily be promoted to the conduction band. Electrons make the major contribution in the conduction of electricity and are called majority carriers, while holes make a small contribution and are the minority carriers.

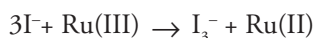
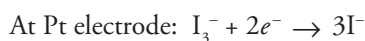
On doping silicon with gallium or indium having three valence electrons, p-type semiconductors with holes as the majority carriers is formed.

On irradiating semiconductor devices with photons, electrons are promoted from the valence band to the conduction band creating electrons and holes. On connecting them to an external load, current can be obtained.

Semiconductors like TiO_2 , ZnO , SnO_2 and Nb_2O_5 have relatively wide energy gaps and hence do not absorb visible light. In such semiconductors, electrons can be excited to the conduction band by adsorbing organic dye on the surface of the semiconductor. Such photovoltaic cells are called *dye-sensitised solar cells*. To prepare such a photovoltaic cell, a glass support is covered with a conducting layer of tin-doped indium oxide (ITO). Nanoparticles of TiO_2 coated with a Ru(II) based sensitising dye is deposited on it. On irradiation with light, the dye is photoexcited and the electrons are injected into the conduction band of the semiconductor.



The electrons flow from the ITO electrode to the Pt counter electrode through the external circuit. A mediator, an organic solvent containing iodide/tri-iodide couple is employed to reduce Ru (III) to Ru (II).



In this process, electrical energy is produced without any permanent chemical changes.

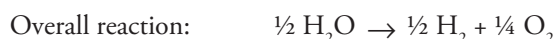
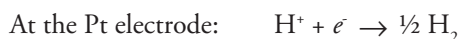
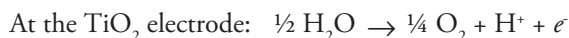
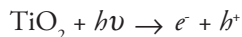
The efficiency of the cell depends upon the ease with which the dye (photosensitiser) absorbs radiation and is excited.

Other applications of semiconductor photochemistry are given below.

- *As sensitisers for water splitting* Hydrogen is considered as a clean and environment friendly fuel. It is also regarded as a renewable energy source as it can be obtained by splitting water which is abundantly available.

Water can be split into hydrogen and oxygen by using semiconductor electrodes like titanium oxide (rutile) and a platinum counter electrode. The TiO_2 electrode is placed in an alkaline solution and the Pt counter electrode in an acidic solution. These two solutions are separated by a porous plug to prevent them from mixing. When TiO_2 is irradiated with UV light, electrons are produced, water is split and hydrogen is released at the platinum electrode (Fig. 18.3).

The reactions are as follows.



Similarly, water can be split by irradiating the semiconductor electrode SrTiO_3 with near UV light of 388 nm. The cell is represented as $\text{SrTiO}_3 // \text{H}_2\text{O} / \text{Pt}$. Other semiconductors that can be used for photosensitised splitting of water are CaTiO_3 , Ti_2O_5 and ZrO_2 .

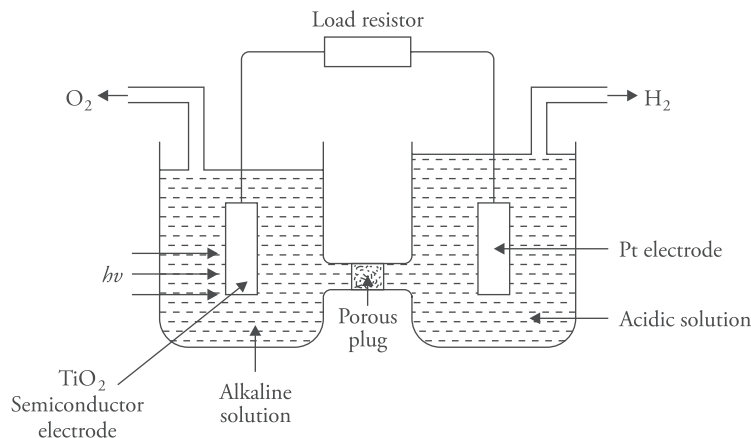
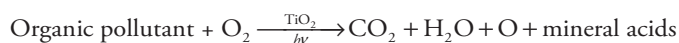


Figure 18.3 Photosensitised splitting of water using TiO_2 semiconductor electrode

Semiconductor photocatalysis

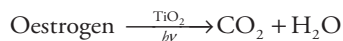
Semiconductors act as excellent photocatalysts and photosensitisers for the breakdown and removal of pollutants. In the presence of light radiations, they adsorb organic pollutants and oxygen and catalyse the oxidative breakdown of these pollutants or other pollutants like volatile organic compounds in air.

TiO_2 being non-toxic and inert serves as an excellent photosensitiser for water treatment.

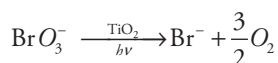


The above process is also called *photomineralisation*. Other common examples of removal of pollutants in the presence of semiconductor TiO_2 are given below.

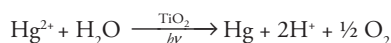
- Various insecticides, pesticides, herbicides, detergents and chemicals undergo photocatalytic degradation.
- It converts the female sex hormone oestrogen present in water into harmless carbon dioxide and water.



- Disinfection of water by chlorination produces carcinogenic compounds. If water is sterilised by chlorination, carcinogenic BrO_3^- ions are produced. These are removed by photosensitisation in the presence of TiO_2 .



- Heavy metals like mercury can be removed from water; they deposit on the surface of the photocatalyst.



- TiO₂ is used for the destruction of malignant cancer causing cells. It is applied as fine particles on the tumour site and then irradiated using an optical fibre.

Semiconductor induced superhydrophilicity TiO₂ exhibits strong hydrophilic nature on irradiation. If glass is coated with TiO₂, the electrons generated on irradiation reduce TiO₂ to Ti (III) species which is hydrophilic. The process is reversible under dark conditions when Ti (III) is oxidised to hydrophobic Ti (IV) (Fig. 18.4).

This property helps glass to clean itself during rainfall. If TiO₂ is coated on it and it is irradiated, then due to the hydrophilic nature of TiO₂, water spreads uniformly. This property also finds use in antifogging lamps and windows where under fogging conditions, water does not form droplets; rather it spreads uniformly as a thin layer of water.

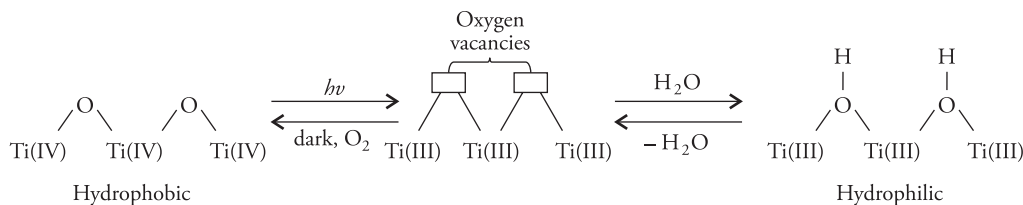


Figure 18.4 Photoinduced superhydrophilicity of TiO₂

Adopted from A Mills and SK Lee, 'A webbased overview of semiconductor photochemistry – Based on current commercial applications', *Journal of Photochemistry and Photobiology A*, 152(2002)© Elsevier.

18.11 Supramolecular Chemistry

A supramolecule is not a molecule in the conventional sense; rather, it is a system or an assembly of two or more entities held together by forces other than the normal covalent bonds. They are held by weak non-covalent intermolecular interactions like hydrogen bond interactions, hydrophobic forces, cation- π interactions, π - π stacking, etc. Supramolecular chemistry deals with the chemistry of such molecules. The bonding interactions between supramolecules are far weaker than covalent bonding, therefore, supramolecular assemblies are weaker than molecular compounds. However, they have high energies and the interactions are orientation dependent. Two important concepts of supramolecular chemistry are

- Molecular self assembly
- Host guest chemistry

1. Molecular self assembly

It is the spontaneous and reversible association of two or more components to form a larger, non-covalently bonded aggregate. DNA is the best example of a self-assembling structure that exists in double helical form in which the two strands are held by hydrogen bonds (Fig. 18.5). Other common examples are surfactant molecules such as detergents which aggregate or self assemble to form spherical micelles (Fig. 18.6). Similarly, liquid crystals aggregate to form the mesogenic phase.

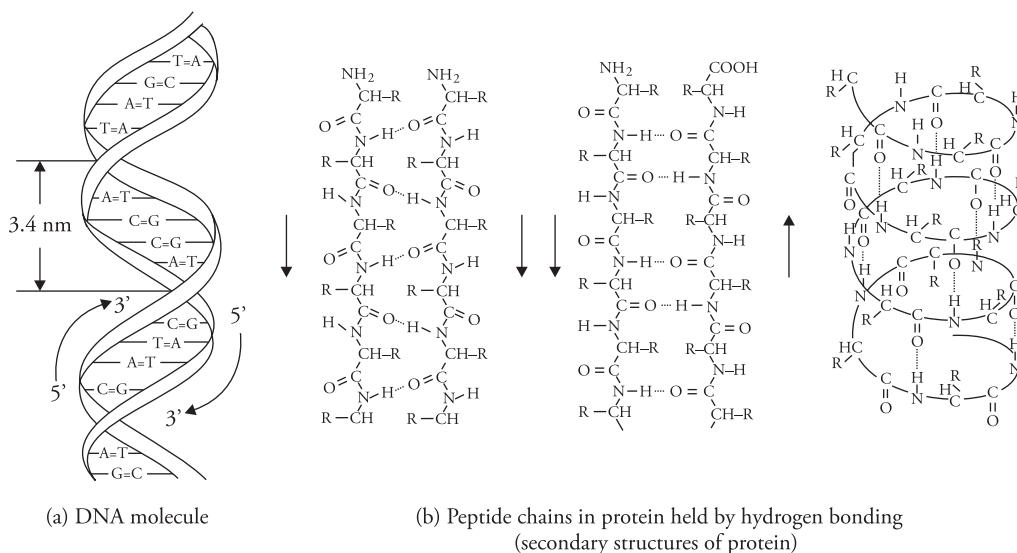


Figure 18.5 Self assembly between complementary molecules

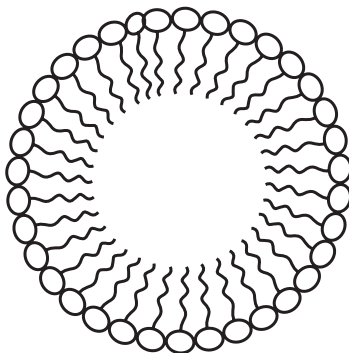


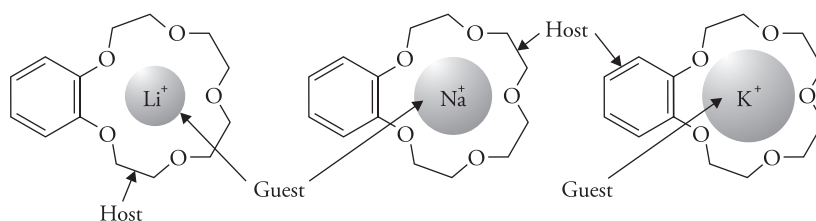
Figure 18.6 A micelle formed by aggregation of surfactant molecules

2. Host–Guest Chemistry

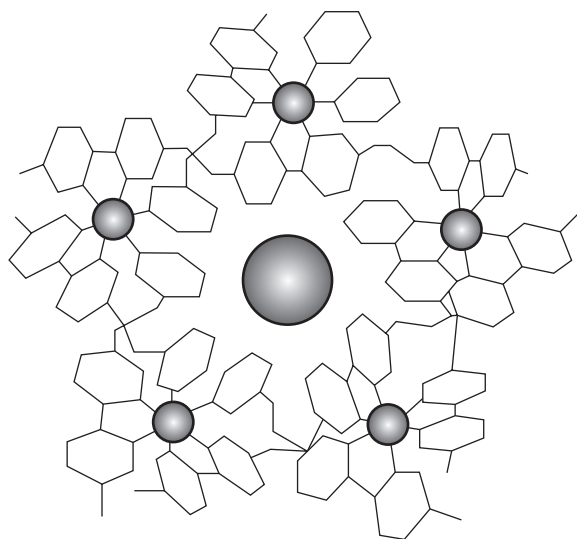
The analogy of host–guest chemistry can be drawn from the enzyme substrate interaction which occurs in the form of a lock and key. The key occupies the hole inside the lock without

any kind of bond formation. In host–guest chemistry, molecular assemblies which are larger molecules act as hosts and entrap small molecules or ions as guests in their cavity via non-covalent interaction. In the enzyme structural model, the receptor or ‘host’ molecule forms a stable complex with one or more ‘guest’ molecules through weak directional forces like hydrogen bonds, van der Waals interactions, electrostatic interactions, hydrophilic and hydrophobic interactions and π -stacking interactions. These forces will operate effectively if the size and shape of the guest molecule matches that of the host. Some examples of host–guest molecules are shown in Figure 18.7.

The chemistry dealing with such molecules was termed as ‘host–guest chemistry’ by Cram (1974) and ‘supramolecular chemistry’ by Lehn (1988).



Na, K, lithium ions inside a crown ether

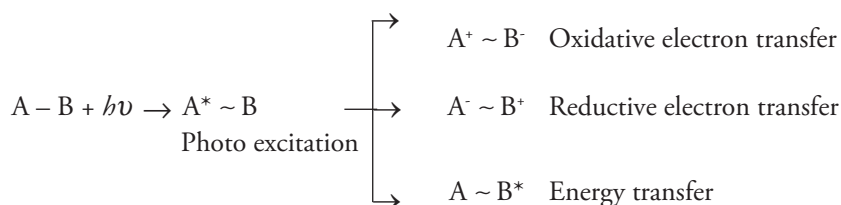


A supramolecular assembly holding a cation

Figure 18.7 Some examples of host–guest molecules

18.12 Supramolecular Photochemistry

Let us consider a supramolecular system as being a dyad, that is, a compound of two components or sub-units $A \sim B$. When this system is irradiated, a photon is absorbed either by a supramolecule or by a component of the supramolecular assembly (say A) and it gets excited to a higher energy level which is unstable. This photoinduced excitation of a specific subunit can modify the electronic transition between the other components of the supramolecular assembly. Photoinduced energy transfer and electron transfer processes can also take place between the two components of the supramolecular species as shown below.



A supramolecular system is composed of several molecular components. Successive energy or electron transfer steps may lead to energy migration or charge separation over long distances. Such transfers are useful in making photochemical molecular devices and can be exploited for various practical purposes like

- Energy transfer
- Signal transfer
- Luminescence for sensors
- Photo-catalysis (multi-electron process)
- Molecular wires
- Electronic devices like light harvesting antennae
- Conduction of an electrical impulse (an electron) between two components

Applications of supramolecular photochemistry

Photoactive guest molecules when placed inside host molecules like micelles, cyclodextrins and zeolites modify the physical and chemical processes of their excited states. This can be illustrated with the help of the following examples.

1. Micelles

Surfactant molecules, above the critical micelle concentration (CMC) self assemble to form spherical micelles with cavities of the order of 1–3 nm diameter. The guest molecules incorporated in these cavities absorb photons and provide the necessary activation to break the covalent bonds in the guest molecules and yield products different from the products obtained by normal pathways.

The products obtained by the normal photolysis (scheme *a* in Fig. 18.8) and photolysis when carried out in the presence of a micelle host (from cetyltrimethylammonium bromide) are different (scheme *b* in Fig. 18.8)

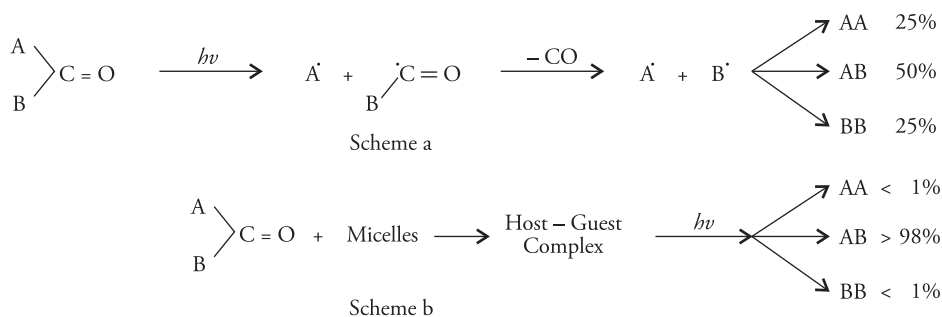


Figure 18.8 Scheme a: products obtained by the normal photolysis
 Scheme b: products formed when photolysis is carried out in the presence of micelle host

2. Photochemical transformations with zeolites as supramolecular hosts

Zeolites are aluminosilicate materials with extensive cavities inside them. A photoactive guest molecule of suitable size and shape gets entrapped in these cavities. It undergoes photoexcitation forming products. The photochemistry and resulting products in normal photochemical reactions and reactions using supramolecules are very different.

Zeolites are used in the field of sunscreens. Sunscreens act as filters of UV-A and UV-B radiations. However, they contain p-aminobenzoic acid (PABA) and its derivatives which can damage DNA due to the formation of singlet oxygen. PABA can be encapsulated on the addition of zeolite, thereby decreasing its harmful effects without affecting its photo-protecting ability.

These days, sunscreens with an organic filter molecule mixed with light scattering metal oxides like TiO_2 or ZnO are becoming very popular. However, the photocatalytic properties of metal oxides degrade the organic molecule and it loses its ability to act as a UV filter. Encapsulating the organic molecule inside a zeolite host prevents it from interacting with the metal oxide as well as the skin, yet retaining its ability to filter UV radiations.

3. Cyclodextrin supramolecular hosts

Cyclodextrins are cyclic oligosaccharides of glucose having (α -1-4) linked α -D glucopyranose units. They contain a lipophilic central cavity and a hydrophilic outer surface (Fig. 18.9). Guest molecules can easily be accommodated inside this cavity. Cyclodextrins have the ability to enhance the luminescence of molecules entrapped in their cavity. Polynuclear aromatic hydrocarbons when present as such in solutions show no phosphorescence but when they are encapsulated with 1, 2-dibromoethane in cyclodextrins and nitrogen gas is passed, they exhibit intense phosphorescence at room temperature. This is because inside the host molecule, the deactivation of the excited triplet state by collision is greatly reduced.

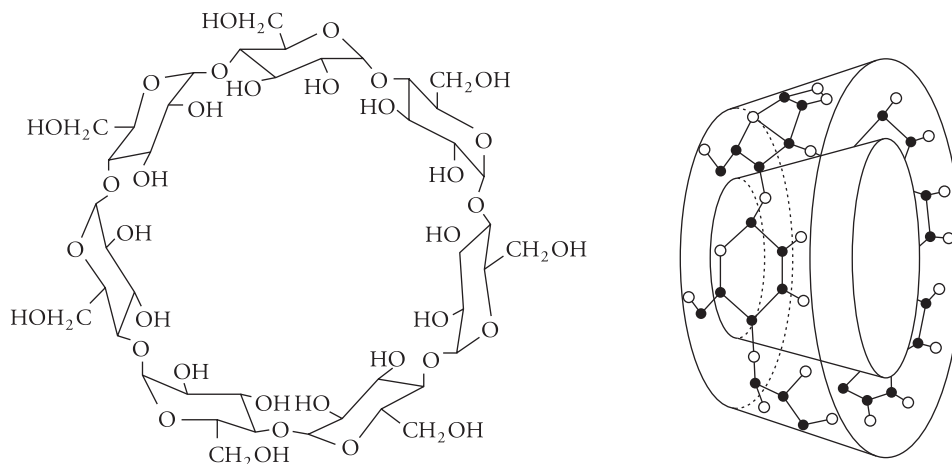


Figure 18.9 The chemical structure and the molecular shape of β -cyclodextrin (β CD)

4. Role of supramolecular photochemistry in vision

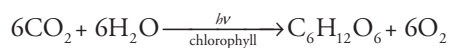
Retina of our eyes contains two type of cells – rods and cones. The rods are receptors for black and white light and function in dim light, whereas cones are sensitive to coloured light. In the rods, the pigment rhodopsin containing the protein opsin absorbs light. The protein molecule is a large molecule which acts as a host for the small guest molecule of chromophore 11-cis retinal held by the protein molecule through non-covalent bonds, that is, by intermolecular forces. The protein modifies the light absorption pattern of 11-cis-retinal which absorbs in ultraviolet region when free and in the visible region when attached to opsin.

When light falls on the retina, 11-cis-retinal absorbs a photon and undergoes photo-isomerisation into 11-trans-retinal, a geometrical isomer. This photo-isomerisation brings about structural changes inside the cavity of the supramolecule resulting in the generation of an electrical signal sent to the brain.

Cones which are responsible for colour vision are of three types corresponding to red, blue and green wavelength. The chromophore is the same 11-cis retinal which is bound to a protein structurally similar to opsin.

5. Photosynthesis

Photosynthesis is a well-known application of supramolecular chemistry to natural processes where green plants in the presence of the pigment chlorophyll trap carbon dioxide and water to manufacture glucose.



Chlorophyll, a supramolecular system is the primary light absorbing pigment which is contained in chloroplasts. It absorbs in the blue and red region, reflecting the green wavelength. There are two types of chlorophyll – *a* and *b*. Other pigments like carotenoids such as β carotene assist chlorophyll in the light harvesting process.

Chlorophyll (Fig. 18.10) consists of

- A porphyrin ring which is the light absorber.
- A hydrophobic phytol chain which helps the chlorophyll molecule to remain embedded in the photosynthetic membrane.

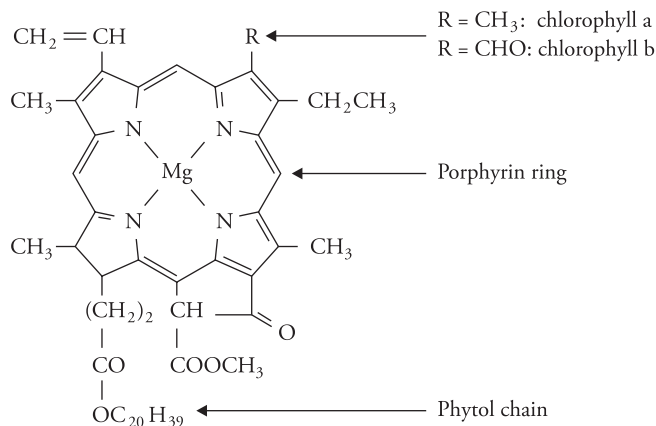


Figure 18.10 Structure of chlorophyll

A series of electron transfer reactions occur in the presence of light (light reactions) followed by reactions in the dark (dark reactions) resulting in the formation of carbohydrates and release of O_2 .

6. Photochemical molecular devices

Supramolecular photochemistry is also used in the design and construction of nano-scale devices such as molecular machines, molecular switches, molecular wires, light harvesting antennas and light conversion devices capable of performing useful light induced functions.

18.13 Introduction to Optical Sensors

Before studying about optical sensors, let us briefly describe an optical fibre. The use of optical fibres for communication is increasing very rapidly. The transmission of light by optical fibres is based on the principle of total internal reflection. An optical fibre is a very flexible glass fibre which transmits optical signals over long distances even if there is no proper alignment between the source and detector.

The optical fibre consists of three parts

- (1) Core (2) Cladding (c) Jacket

The core is the innermost part of the fibre and is made up of either glass or plastic. It is surrounded by the cladding which is also made up of glass or plastic whose refractive index is less than that of the core. The jacket is the outermost plastic sheath which protects the fibre from abrasion, wear and tear.

Optical fibres not only play an important role in communication but are also used in the development of different type of sensors. An optical sensor converts light rays into electronic signals. Fibre optic sensors have high sensitivity. They can easily measure and monitor different physical and chemical parameters in terms of parameters of light beam like light intensity, polarisation and wavelength. They can be used in remote sensing devices and to sense regions that are otherwise inaccessible. Fibre optic sensors have various advantages.

- They are chemically inert.
- They have low weight and volume and are convenient to use.
- They are safe under explosive conditions.
- They are resistant to nuclear or ionising radiations.
- There is no potential risk of fire or spark.
- They are not affected by external noise.
- The signals travel very fast and have wide band transmission.
- There is no electromagnetic interference in the signal and the signals are not affected by electrical noise.

Classification of optical sensors

Optical sensors can be classified on the

1. Basis of sensor location
 - (i) Extrinsic sensors
 - (ii) Intrinsic sensors
 2. Basis of operating principle
 - (i) Intensity modulated optical sensors
 - (ii) Phase modulated optical sensors
 - (iii) Frequency modulated optical sensors
 - (iv) Polarisation modulated optical sensors
 - (v) Wavelength modulated optical sensors
 3. Basis of application
 - (i) Physical sensors
 - (ii) Chemical sensors
 - (iii) Bio-medical sensors
1. Based on sensor location
 - (i) *Intrinsic optical sensors* In intrinsic optical sensors, the physical parameters of the light are modulated within the fibre in response to the environmental changes. There can be modulation of intensity, phase, frequency or wavelength of the light signal. Compared to extrinsic optical sensors, these are more sensitive and more expensive. They are used to sense rotation, acceleration, strain, vibration or acoustic pressure.

- (ii) *Extrinsic optical sensors* In extrinsic sensors, the modulation of light takes place outside the fibre. The fibre simply acts as an information/light carrier to and from the sensor head. They are less expensive and less sensitive compared to intrinsic sensors. They find use in sensing temperature, pressure, liquid level and flow.
2. Based on operating principle
 - (i) *Intensity modulated optical sensors* In this type of sensors, the intensity of light wave is modulated in response to environmental changes. Intensity modulation is the cheapest and simplest way of detecting and measuring different parameters. They find use in medical catheters like cardiac pressure transducers, etc.
 - (ii) *Phase modulated optical sensors* These sensors are very sensitive and are based on optical phase modulation. When a light beam passes into the interferometer, it splits into two beams, one of which is exposed to the sensing environment and the other is isolated from the environment and serves as the reference beam.
 - (iii) *Frequency modulated optical sensors* These sensors modulate the frequency of light waves.
 - (iv) *Polarisation modulated optical sensors* This is an important class of sensors and is used to measure a range of parameters. The direction of polarisation of electric field is modulated in response to the environmental changes.
 - (v) *Wavelength modulated optical sensors* In these sensors, the wavelength of the light ray undergoes modulation.
 3. Based on application
 - (i) *Physical sensors* Physical parameters like temperature, pressure and distance are sensed.
 - (ii) *Chemical sensor* They help to measure concentration and activity of a chemical species in a sample.
 - (iii) *Bio-medical sensor* They help to sense disorders in biological systems, flow of blood, degree of arteriosclerosis in arteries, etc.

Applications of optical sensors

Optical sensors have a variety of uses

1. They are used to measure vibration, rotation, displacement, torque, twisting, acceleration, etc.
2. Infrared sensors help in measuring temperature without physical contact with the object.
3. They help to sense surface roughness and thickness.
4. In the biomedical field, they help to probe internal organs.
5. They are used to monitor structures like bridges, buildings, dams, tunnels, monuments, dykes, pipelines, etc.
6. In biometrics, optical sensors can scan fingers, face, eyes and can process images.
7. Optical sensors find use in night vision cameras.
8. They are used in military and law enforcement activities.

Summary

- Photochemistry deals with the chemical effects produced by light radiation in the wavelength range 2000–8000 Å.
- In photochemical reactions, the activation energy of the molecules is received by light radiations. The reaction can occur spontaneously both with increase and decrease in free energy.
- Two laws govern photochemical reactions.
 - (i) Grotthuss–Draper law: It states that the chemical reaction is brought about by that portion of the incident light which is absorbed.
 - (ii) Stark–Einstein law of photochemical equivalence: It states that each molecule absorbs one quantum of light, gets activated and induces the reaction.
- A photochemical reaction proceeds in two steps. In the first step, called the primary process, it absorbs light and gets activated. In the second step, called the secondary process, the activated molecules undergo chemical reaction.
- Quantum yield (Φ) is defined as the number of molecules reacted or formed per photon of light absorbed.

$$\text{Quantum yield } \Phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of photons absorbed in the same time}}$$

- Quantum yield of a reaction is unity if one quantum of light causes one molecule to react or decompose. It can also be greater than or less than one.
- If a molecule after absorbing light in the primary process initiates a chain reaction in the secondary step or the free radicals produced in the primary step attack another reactant molecule in the secondary step, then the quantum yield of the reaction is greater than one.
- If the molecule activated in the primary step recombines forming a reactant or gets deactivated by collision or loses energy by fluorescence, then the quantum yield of the reaction is less than one.
- The electrons of a reactant molecule on absorbing photochemical energy get excited without spin inversion so that the molecule remains paired in the excited state. This is called the singlet state. When the electron from an excited singlet state returns to the ground state, it emits radiation called fluorescence.
- The electron in the excited singlet state undergoes spin inversion going to a new excited state called the triplet state. The triplet state is more stable than the singlet state. When the electron from the triplet state returns to the ground state, it emits radiation called phosphorescence.
- Both fluorescence and phosphorescence are photophysical processes.
- Jablonski diagram represents the excitation of electrons on absorption of energy and their consequent decay to the ground state, emitting fluorescence and phosphorescence.

- When chemical reactions are accompanied by the emission of visible light it is called chemiluminescence.
- Certain living organisms like fire flies also exhibit chemiluminescence due to aerial oxidation of some proteins. This is called bioluminescence.
- Photosensitisation is the process in which a molecule gets excited on absorbing light and stimulates other molecules which cannot absorb light directly.
- Certain semiconductors like Si, TiO_2 , ZnO and SrTiO_3 when irradiated absorb light and the electrons are promoted to the conduction band. They find use in photovoltaic cells as sensitisers for water splitting, in photo-catalysis and also in inducing superhydrophilicity.
- Optical sensors convert light rays into electronic signals. They are based on optical fibre technology and are widely used as pressure sensors to indicate oil and gas levels, distance sensors to determine distance, fibre optic sensors, in testing instruments, automatic doors, etc.
- A supramolecule is not a conventional molecule but an assembly of two or more entities held together by non-covalent intermolecular associations like hydrogen bond interaction, van der Waals forces, dipole–dipole interaction, hydrophobic forces, cation– π interactions and π – π stacking.
- In host–guest chemistry, the large molecular assembly behaves as a host and the smaller molecule gets trapped in the cavity of the host as a guest via non-bonded interaction.
- Supramolecular photochemistry finds use in photochemical transformation with micelles, zeolites, cyclodextrins, and in natural processes like vision and photosynthesis.

Review Questions

1. What are photochemical reactions? Differentiate between photochemical and thermochemical reactions.
2. Explain the different laws of photochemistry.
3. Derive the Beer–Lambert law governing the absorption of light in photochemical reactions.
4. What is quantum yield? Explain why in certain cases, the quantum yield is higher or lower than that expected from the law of photochemical equivalence.
5. Write short notes on the following.
 - (i) Grotthuss–Draper law.
 - (ii) Stark–Einstein law of photochemical equivalence.
 - (iii) Beer–Lambert law.
 - (iv) Primary and secondary photochemical reactions.
 - (v) Quantum yield.

6. What are excited singlet and triplet states? Explain the phenomenon of fluorescence and phosphorescence with the help of a Jablonski diagram.
7. Differentiate between fluorescence and phosphorescence. Explain the various applications of both the phenomenon.
8. What is photosensitisation? Explain with the help of a suitable example.
9. What is semiconductor photochemistry? Explain the various applications of photosensitisation reactions of semiconductors.
10. What are supramolecules? Explain their photochemistry and various applications.
11. What are optical sensors? Classify the different types of optical sensors and give their applications.

Multiple Choice Questions

1. The chemical effects produced by light radiations chiefly in visible and ultraviolet region is
 - (a) Thermochemistry
 - (b) Electrochemistry
 - (c) Photochemistry
 - (d) Nanochemistry
2. Photochemical reactions occur spontaneously with
 - (a) Decrease in free energy
 - (b) Increase in free energy
 - (c) Both increase and decrease in free energy
 - (d) Neither increase nor decrease in free energy
3. When light is incident on any substance, only that portion of the incident light which is absorbed is effective in bringing about photochemical reactions. The reflected and transmitted light play no role in the reaction. This was stated by
 - (a) Grotthuss and Draper
 - (b) Stark and Einstein
 - (c) Beer and Lambert
 - (d) Kohlrausch
4. The ratio of the number of molecules reacting in a given time and the number of photons absorbed in the same time is termed as
 - (a) Quantum yield
 - (b) Quantum efficiency
 - (c) Both (a) and (b)
 - (d) Quantum number
5. The range of radiations usually used for photochemical reaction is
 - (a) 2000–4000 Å
 - (b) 2000–8000 Å
 - (c) 6000–8000 Å
 - (d) 4000–6000 Å
6. The energy contained in one einstein is
 - (a) $E = h\nu$
 - (b) Nhc/λ
 - (c) $Nh\nu/c$
 - (d) Nhc/ν

7. The quantum yield for the reaction $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ is
(a) 1 (b) Less than one
(c) 3 (d) 10^4 to 10^6
8. When an electron in the excited singlet state returns to the ground state by emitting radiation, the phenomenon is called
(a) Chemiluminescence (b) Fluorescence
(c) Phosphorescence (d) Bioluminescence
9. The excitation of a molecule without spin inversion gives rise to the
(a) Singlet excited state (b) Triplet excited state
(c) Both a and b (d) None of the above
10. The phenomenon in which a molecule absorbs light radiations and activates another molecule which is itself incapable of absorbing light energy by the transfer of energy is called
(a) Fluorescence (b) Phosphorescence
(c) Photosensitisation (d) Photoexcitation
11. The common applications of semiconductors in photochemistry are
(a) Photovoltaic cells (b) Photocatalysts
(c) Sensitisers for water splitting (d) All of the above
12. Host–guest chemistry is another term for
(a) Supramolecular chemistry (b) Supermolecular chemistry
(c) Semiconductor chemistry (d) Optical sensor technology
13. Interactions not found in supramolecules are
(a) Dipole–dipole interaction (b) Covalent bond interaction
(c) $\pi - \pi$ stacking (d) van der Waals forces
14. Which of the following molecule will not self assemble to form a supramolecule?
(a) Micelles (b) Zeolite
(c) Cyclodextrins (d) Water

Solution

- | | | | | | | | |
|-------|--------|--------|--------|--------|--------|-------|-------|
| 1 (c) | 2 (c) | 3 (a) | 4 (c) | 5 (b) | 6 (b) | 7 (d) | 8 (b) |
| 9 (a) | 10 (c) | 11 (d) | 12 (a) | 13 (b) | 14 (d) | | |

Chapter 19

FUNDAMENTALS OF ORGANIC CHEMISTRY

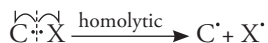
19.1 Introduction

Organic chemistry is defined as the study of compounds of carbon or the chemistry of hydrocarbons and its derivatives. The term 'organic' is misleading. Earlier the term **organic chemistry** was used to describe the study of compounds obtained from living organisms, while the term inorganic chemistry was used for the study of compounds obtained from non-living sources. With the synthesis of urea, the first organic compound synthesised in the laboratory, it was proved that organic compounds can also be prepared artificially. Urea was synthesised from an inorganic compound, that is, from ammonium cyanate (NH_4CNO). Later on Kolbe (1845) succeeded in preparing acetic acid, the first organic compound synthesised in laboratory from its elements. Today most of the organic compounds can be synthesized. The division between organic and inorganic is retained till date. Presently, the term organic is used to describe the compounds of carbon. Carbon atoms have a unique property of attaching themselves to one another to an extent not possible for atoms of any other element. This property is called 'catenation'. The carbon atoms can form long chains (linear, branched and cross link) or rings of all sizes. Organic molecules have 'covalent bonds' formed by the sharing of electrons between the bonded atoms. Covalent bonding imparts properties to organic compounds which are quite different from those of inorganic compounds. The general concepts and principles underlined in the forthcoming sections will give a better understanding of the organic compounds, their mechanism of bond cleavage and organic reaction mechanisms.

19.2 Cleavage of Covalent Bonds

Organic reactions involve breaking and formation of covalent bonds. It is essential to understand the ways in which a covalent bond can break. A covalent bond generally breaks in two ways depending on the nature of organic compound, nature of attacking reagent and the reaction conditions. The different possibilities are illustrated below:

- (i) **Homolytic cleavage** As we know, a covalent bond is formed by sharing of electrons between the two atoms. In a homolytic cleavage, the bond breaks symmetrically in such a way that each species retains one electron of the shared pair.



where C represents carbon atom, X represents side group and \curvearrowright represents single electron transfer.

Homolytic cleavage thus results in the formation of highly reactive neutral species containing odd or unpaired electrons. Such species are known as free radicals. The reactions which proceed by the formation free radicals are known as free radical reactions. Homolytic cleavage occurs when the electronegativity of the bonded atoms is the same, that is, both the bonded atoms have equal attraction for the shared electron pair.

- (ii) **Heterolytic cleavage** When the electronegativities of the bonded atoms is different, one atom has greater attraction for the electron pair than the other; unsymmetrical bond cleavage occurs. This can take place in two different ways.

- (a) If X is more electronegative than carbon, then X retains the electron pair, leaving C positively charged.



where the curved arrow \curvearrowright represents the transfer of both electrons.

This carbon bearing a positive charge is called the carbonium ion or carbocation.

- (b) If X is less electronegative than carbon then the carbon atom retains the electron pair.

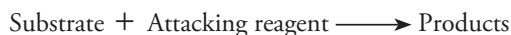


The carbon atom bearing the negative charge is called the carbanion.

Reactions which proceed by the formation of carbocations or carbanions are called ionic reactions.

19.3 Attacking Reagents

When a chemical reaction takes place between two substances, one of them is treated as the substrate and the other is the attacking reagent. The substrate forms the product in the presence of the attacking reagent.



Substrate and attacking reagent are relative terms. A substance can be attacking reagent in one reaction and substrate in the other. The substance due to whose presence the substrate undergoes a change is the attacking reagent.

There are generally two types of attacking reagents

- (i) Electrophilic reagents or electrophiles
- (ii) Nucleophilic reagents or nucleophiles
- (i) **Electrophiles or Electrophilic Reagents** (*electro*: electron; *philic*: loving). Electrophiles are electron-loving species which have an incomplete octet and attack electron-rich species. Such reagents can accept an electron pair and hence they are also known as lewis acids.

An electrophile can be either a positively charged species or a electrically neutral species having an incomplete octet.

- (a) **Positive electrophiles** They are electron-deficient species which carry a positive charge.

Some common examples of positive reagents are H^+ , H_3O^+ , Cl^+ , NO_2^+ , NO^+ , R^+ , etc.

- (b) **Neutral electrophiles** They are those species which have six electrons in their outermost orbit. They require an electron pair to complete their octet and acquire a stable configuration. Hence they are also electron loving and attack electron-rich species. Some common examples are BF_3 , FeCl_3 , AlCl_3 , ZnCl_2 , carbenes, nitrenes, etc.

- (ii) **Nucleophiles or Nucleophilic Reagents** (*nucleo*: nucleus; *philic*: loving). Nucleophiles are electron-rich species having an unshared pair of valence electrons. They attack electron-deficient sites. Being electron pair donors, they can also be termed as lewis bases.

A nucleophile can be either neutral or negatively charged species.

- (a) **Negative nucleophiles** These are electron-rich species carrying a negative charge. Some common examples are Cl^- , Br^- , I^- , OH^- , OR^- , NH_2^- , CN^- , COO^- , HSO_3^- , R^- (carbanion), RCOO^- , etc.

- (b) **Neutral nucleophiles** They are electron-rich species having a lone pair of electrons, but they carry no charge. Examples include $\text{H}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{S}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{R}$, etc.

The electron-rich species O, S, etc., donate electrons and attack the electron-deficient centres.

Table 19.1 Difference between electrophiles and nucleophiles

Electrophiles	Nucleophiles
1. They are electron-deficient species which can accept an electron pair.	They are electron-rich species which donate an electron pair.
2. Electro: electron; philic: loving. They are electron loving species and attack electron-rich centre.	Nucleo: nucleus; philic: loving. They are nucleus loving species and attack areas of low electron density.
3. They can be positively charged or neutral species having six electrons in their valence shell.	They can be negatively charged or neutral species with a lone pair of electrons.
4. They are lewis acids and can accept an electron pair	They are lewis bases and donate an electron pair
5. Example: BF_3 , AlCl_3 , H_3O^+ , Cl^+ , NO^+ , R^+ , etc.	Example: $\text{H}\ddot{\text{O}}\text{H}$, $\text{R}\ddot{\text{O}}\text{H}$, Cl^- , Br^- , OH^- , CN^- , etc.

Practice problems

- Classify the following into electrophilic and nucleophilic reagents
 (a) H^+ (b) Cl^- (c) NO_2^+ (d) OH^-
- Which of the following molecules or ions is electrophilic
 CH_4 , H_2O , Br^+ , $\text{CH}_2=\text{CH}_2$, BF_3 , NO_2^+ , NH_3
- Which of the following molecules and ions are nucleophilic
 CH_4 , H_2O , BH_3 , OH^- , Br^+ , NH_3 , AlCl_3

19.4 Electron Displacements in Covalent Bonds

Organic compounds mainly consist of covalent bonds. The electron pair of these covalent bonds may undergo displacement either due to different substituents attached in the molecule or under the influence of the attacking reagents (nucleophile or electrophile). The displacement of electrons develops polarity in the molecule. These electron displacements can be temporary or permanent. Temporary electron displacements occur under the influence of attacking reagents and disappear as soon as the attacking reagent is removed. These effects are known as **polarisability effects**. Permanent electron displacements occur under the influence of substituents within the molecules. They are known as **polarisation effects**.

Permanent and temporary effects are also denoted as static and dynamic effects respectively. Some important displacement effects are-

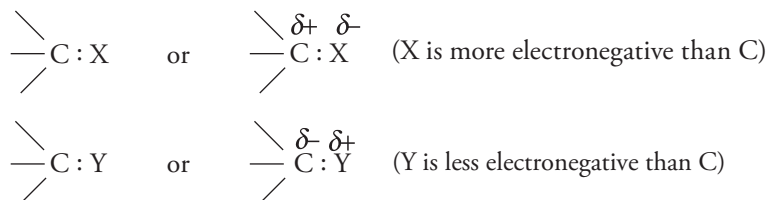
- Inductive effect
- Mesomeric effect
- Electromeric effect
- Inductomeric effect
- Hyperconjugation

Let us now discuss these static (permanent) and dynamic (temporary) effects one by one.

Inductive effect A covalent bond is formed by the sharing of electrons between the two bonded atoms. If the electronegativities of the two atoms is similar the electron pair will occupy a central position between the two nuclei of the concerned atoms. Such a covalent bond is termed as non-polar covalent bond. For example



On the other hand, if a covalent bond is formed between two dissimilar atoms having different electronegativities, then the electron pair will be attracted towards the more electronegative atom. Consequently a partial negative charge (denoted by δ^-) will develop on the more electronegative atom, and a partial positive charge (denoted by δ^+) will develop on the less electronegative atom. Consequently there is polarisation of the molecule. This polarisation is of a permanent nature.



Here, it is important to note that although the electron pair is permanently displaced, it remains in the valence shell.

This permanent creation of a dipole between a carbon atom and the atom or group to which it is attached is called the inductive effect or simply I effect.

If the substituent group is more electronegative than carbon atom and attracts the electron pair towards itself, it is said to exert $-I$ effect or negative inductive effect.

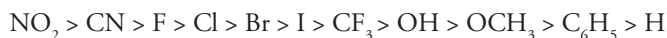
On the other hand if the substituent is electron releasing it is said to exert $+I$ effect or positive inductive effect.



Inductive effect is represented by the symbol \longrightarrow , the arrow pointing towards the more electronegative element or group.

Some groups in the order of decreasing inductive effects are

(i) $-I$ effect groups (electron attracting or electron withdrawing)



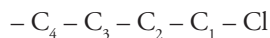
(ii) $+I$ effect groups (electron repelling or electron releasing)



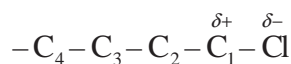
The values of dipole moments are a measure of the degree of inductive effect.

Inductive effect is transmitted along the chain of carbon atoms and its effect decreases rapidly with the length of the carbon chain. This can be understood with the help of the following example.

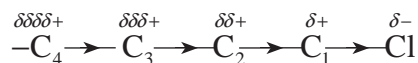
Consider a carbon chain with chlorine atom attached to the terminal carbon atom.



Being more electronegative than carbon, the chlorine atom pulls the bonded electron pair towards itself. As a result, chlorine develops a partial negative charge and the carbon atom C_1 acquires a small positive charge.

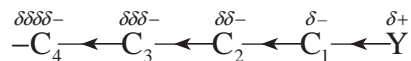


As C_1 is positively charged, it attracts the electron pair between C_1 and C_2 towards itself. As a result, C_2 acquires a small positive charge whose magnitude is smaller than the charge on C_1 . C_2 will further attract the electron pair between C_2 and C_3 towards itself, as a result of which C_3 will acquire a small positive charge. The magnitude of positive charge decreases from C_1 to C_2 to C_3 and it is denoted by $\delta+$, $\delta\delta+$ and $\delta\delta\delta+$.



Inductive effect is transmitted along the sigma bonded carbon chain. It is a permanent effect and vanishes after C_3 for all practical purposes.

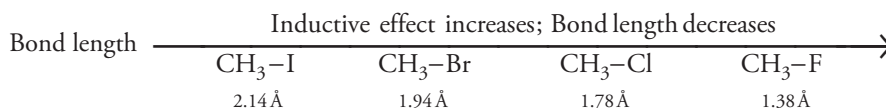
The effect will be reversed if an electron donating group (+I effect) is attached to the carbon atom.



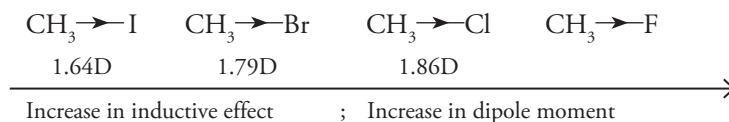
The electron attraction and repulsion are compared with hydrogen as a reference in the molecule CR_3-H as standard.

Inductive effect is a very important effect in organic chemistry and plays a significant role in understanding several reactions. Some common applications of inductive effect are discussed below

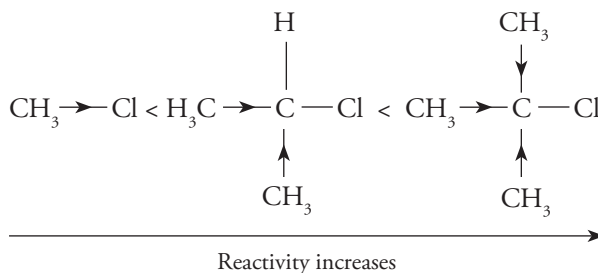
1. **Effect on bond length** Due to inductive effect, the covalent bond develops partial ionic character. Greater the inductive effect greater will be the ionic character and lesser will be the bond length. For example, the bond length of alkyl halides is found to increase with the decrease in inductive effect.



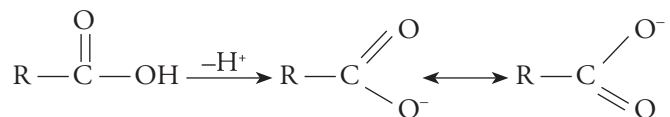
2. **Dipole moment** Molecule develops polar character due to inductive effect. Dipole moment is found to increase with the increase in inductive effect.



3. **Reactivity of alkyl halides** Alkyl halides are more reactive than the corresponding alkanes. They undergo nucleophilic substitution reactions. The formation of stable carbonium ion is facilitated due to +I effect of the methyl groups. Greater the number of methyl groups, more is the inductive effect (+I effect) facilitating the replacement of halogen atom and hence faster is the reaction.

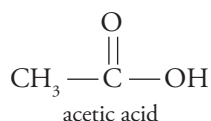
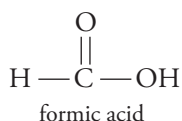


4. **Strength of carboxylic acids** The strength of a carboxylic acid depends on the ease with which it donates a proton. Carboxylic acids release a proton and change into carboxylate ion.

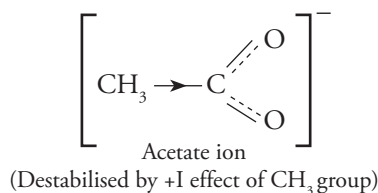
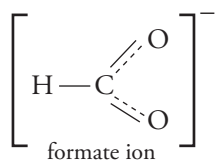


Any factor which stabilises the carboxylate ion increases the strength of the carboxylic acid. Lesser the stability of carboxylate ion weaker will be the carboxylic acid. Inductive effect influences the strength of carboxylic acids as follows.

- (i) **Effect of +I groups** Consider the example of formic acid (HCOOH) and acetic acid (CH_3COOH)



CH_3 group in acetic acid has +I effect (electron donating effect). Hence it will intensify the negative charge on oxygen and destabilise the carboxylate ion. There is no such destabilisation in formic acid. Hence its carboxylate ion is more stable. Hence formic acid is stronger than acetic acid.



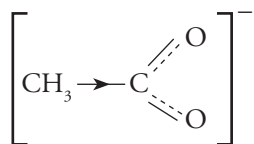
As the +I effect of alkyl groups increases in the order:



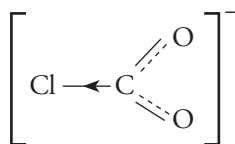
Hence the acidic strength decreases in the same order:



- (ii) **Effect of -I groups** The groups having -I effect will stabilise the carboxylate ion by dispersing the -ve charge on it. For example-



+I effect of $-\text{CH}_3$ group intensifies the negative charge and destabilises the carboxylate ion



-I effect of chlorine atom disperses the negative charge and stabilises the carboxylate ion

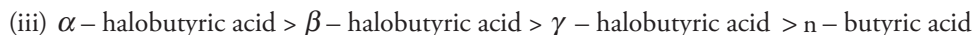
Therefore chloroacetic acid is stronger than acetic acid. The acid strength of halogenated acids is as follows:



–I effect of $\text{F} > \text{Cl} > \text{Br} > \text{I}$



More the number of halogens on the α – carbon atom stronger is the acid.



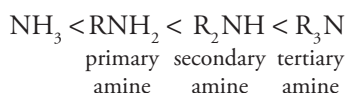
Since the –I effect decreases along the length of the carbon chain, acidic strength reduces.

5. **Basic nature of amines** A base is an electron pair donor. Greater the tendency of a compound to donate electron pair, greater will be its basic character. Amines have a lone pair of electron on nitrogen atom and therefore have a strong tendency to donate an electron pair. Inductive effect influences the basic nature of amines as described below-

- (a) **+I effect** Electron donating groups increase the density of electrons on the nitrogen atom and hence increase the basic strength of the amines.



On the basis of the above description one would conclude that more the number of alkyl groups attached to nitrogen greater will be the basic strength. Hence on the basis of inductive effect, the strength of amines should follow the order



However, the *actual order* of basicity in aqueous solution is

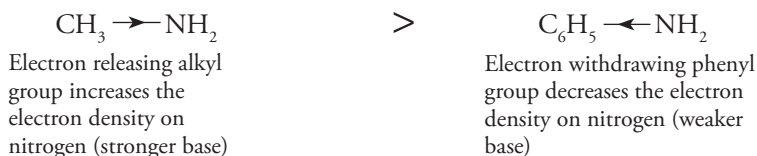
secondary amine > primary amine > tertiary amine > ammonia

This is because apart from inductive effect, steric factor plays a vital role in determining the basic strength of amines. It has been found

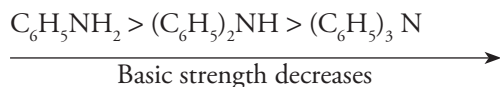


→
Basic strength decreases

- (a) **–I effect** The electron withdrawing groups present on the nitrogen atom in amines decrease the electron density on nitrogen making the electron release difficult. Hence –I groups decrease the basic strength of the amines.



Similarly the basic strength of aromatic amines follows the order

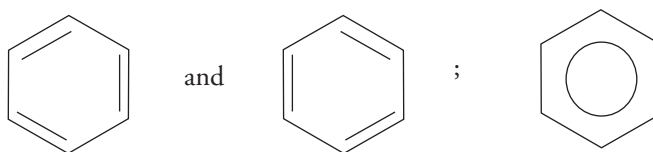


Mesomeric or Resonance Effect

It is a permanent effect in which the π electrons are transferred from a multiple bond to an atom or from a multiple bond to a single covalent bond or from atoms with lone pair of electrons to the adjacent single covalent bond.

To illustrate the above effect let us consider the example of benzene.

The structure of benzene shows that there are three carbon–carbon double bonds and three carbon–carbon single bonds. The bond lengths of the double-bonded carbons should be 1.33 Å and single-bonded carbon atoms should be 1.54 Å. X-ray diffraction studies show that all the six carbon-carbon bonds in benzene are equal and have a bond length of 1.39 Å, which is intermediate between the bond length of single and double bonds. Hence, the structure is symmetrical. This can be explained considering that benzene molecule is a hybrid of the following contributing structures.



The molecule in such cases is said to be in a state of resonance (Heisenberg, 1926) or mesomerism (Ingold 1933)

The structures contributing to the resonance hybrid are indicated by double-headed arrows (\leftrightarrow) and the contributing structures are called the canonical structures.

Like the inductive effect, mesomeric effect may be + or – and is generally denoted by +M or –M.

+ M Effect or +R Effect A group or atom is said to have +M or +R effect if the direction of displacement of electrons is away from it. This effect is generally exhibited by groups having lone pair of electrons.



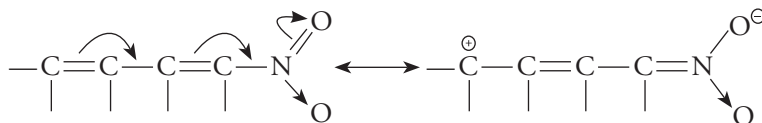
Groups showing + M or + R effect are

Halogens, $\ddot{\text{O}}\text{R}$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{N}}\text{R}_2$ and $-\ddot{\text{S}}\text{R}$

–M Effect or –R Effect A group or atom is said to have a –M or –R effect if the direction of displacement of electrons is towards it. This effect is shown by groups having highly electronegative atoms attached to them.

$> \text{C}=\text{O}$, $-\text{NO}_2$, $-\text{CN}$ groups show –M effect

–M effect of nitro group can be depicted as follows:



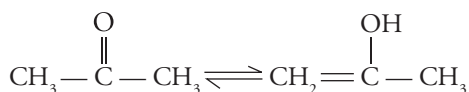
Conditions for Resonance

1. The position of atoms in each of the canonical structures must be the same as in the actual molecule (resonance hybrid). The arrangement of electrons can differ.

For example, vinyl chloride has the following resonating structures

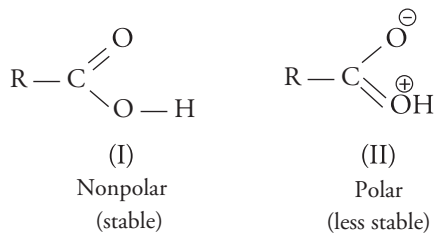


The following structures of acetone are no longer resonating structures because the position of hydrogen has shifted.



They instead represent two different molecules: the *keto* and *enol* forms.

2. The contributing structures are of comparable energy.
3. It is essential that the resonating structures must be planar.
4. There is delocalisation of π electrons.
5. Non-polar structures are more stable than dipolar structures. For example, in the resonating structures of carboxylic acids, structure (I) is more stable than structure (II) although both of them have the same number of bonds.



Resonance Energy

A resonance hybrid is characterised by (i) intermediate bond length, (ii) dispersal of charge and (iii) increased stability.

A resonance hybrid is more stable than any of its contributing (canonical) structures because its energy is lesser than the energy of any of the contributing structures. *This difference in energy between the resonance hybrid and the most stable canonical structure is referred to as the resonance energy of the molecule.*

It has been observed that greater the resonance energy, greater is the stability of the hybrid.

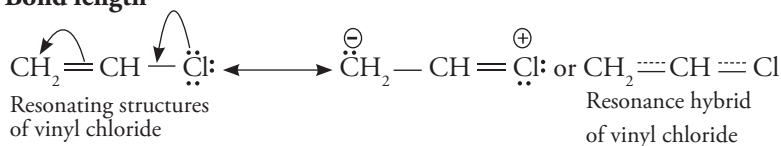
Effects of Resonance

- (a) **Dipole moments** The abnormal values of dipole moments of some molecules can be explained by resonance. The dipole moment value of vinyl chloride can be explained only if structure (II) contributes to the actual structure of the molecule.



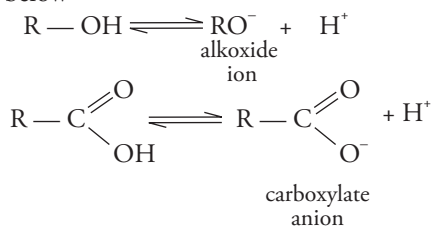
dipole moment $\mu = 1.44 \text{ D}$

- (b) **Bond length**

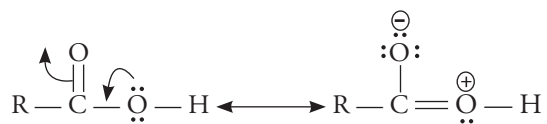


The C-Cl bond length (1.72 Å) in vinyl chloride is shorter than in ethyl chloride (1.78 Å). This can be explained by the concept of resonance. Resonance also explains the equal bond length of all the C-C bonds in benzene (discussed earlier)

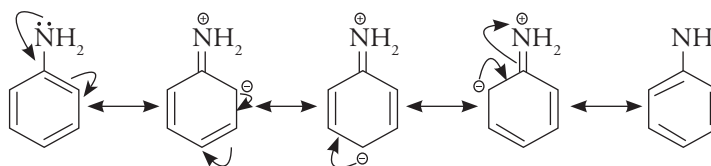
- (c) **Strength of acids and bases** The phenomenon of resonance explains why alcohols are neutral and carboxylic acids are strong acids. The ionisation of alcohols and acids is depicted below



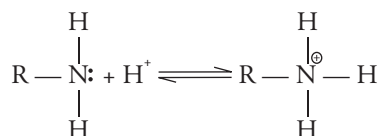
There is no resonance stabilisation in alkoxide ion, whereas carboxylate anion is stable as it is stabilised by resonance. Moreover the resonance stabilisation of carboxylate ion is more than that of the parent acid as in the latter it gets decreased due to charge separation.



Resonance also explains why aromatic amines are weaker bases than aliphatic amines. In aromatic amines the lone pair of electrons on the nitrogen atom is involved in resonance and hence is not easily available for protonation



Therefore, the lone pair of electrons is not available for protonation. In aliphatic amines the lone pair of electrons is very easily available for protonation as the phenomenon of resonance is not possible.



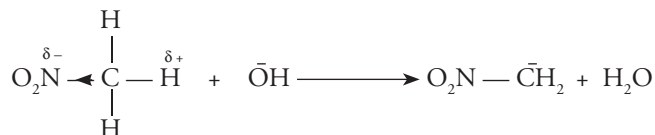
Resonance phenomenon also explains

- Acidic nature of phenols
- Acidity of acetylene

Inductomeric effect

It is a temporary effect and takes place in a sigma bonded system. It enhances the permanent inductive effect by the approach of a charged ion (attacking reagent). In the presence of the attacking reagent the transfer of σ electron cloud takes place readily.

For example, in nitromethane, the $-\text{NO}_2$ group has $-I$ effect. This $-I$ effect of nitro group is further enhanced by $\bar{\text{O}}\text{H}$ group of the base. In the presence of the base, the electron transfer takes place faster and hydrogen is removed as water.



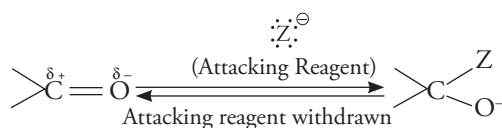
Inductomeric effect always aids a chemical reaction and never inhibits it. Except assisting in the displacement of electrons in inductive effect it does not find any other role in organic chemistry.

Electromeric Effect

Like inductomeric effect, this is also a temporary effect. But unlike inductomeric effect, this takes place between two atoms joined by a multiple bond (π bonded system), that is, double or triple bond ($C = C$, $C = O$, $C \equiv N$, etc.). It is represented by the symbol E and comes into play at the requirement of the attacking reagent. It involves complete transfer of the shared pair of electrons of the multiple bond instantaneously to one of the bonded atoms leading to the development of + and – centres within the molecule.

It is important to note that electromeric effect is temporary in nature and the molecule acquires its original electronic condition on removal of the attacking reagent.

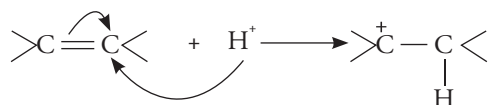
For example, when a negatively charged reagent say $:\ddot{Z}:^{\ominus}$ approaches an aldehyde or ketone, it causes instantaneous shift of electron pair of carbonyl group to oxygen (as it is more electronegative than carbon).



Electromeric effect can be of two types.

+E effect When the transfer of electrons takes place towards the attacking reagent, it is called +E effect

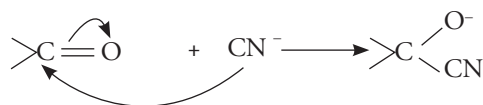
For example



In the above example, the electrons of the double bond are transferred to that atom to which the attacking reagent finally gets attached.

–E effect When the transfer of electrons takes place away from the attacking reagent it is called –E effect.

For example



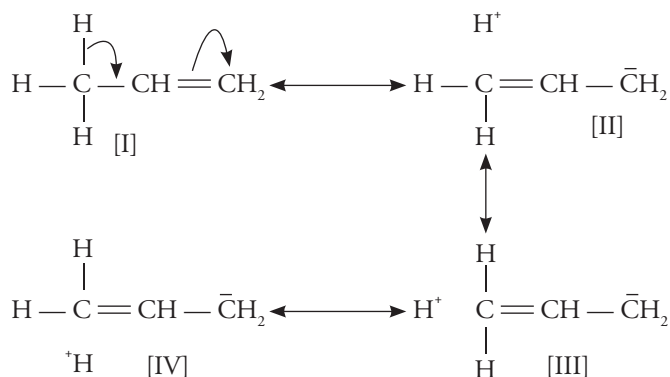
The electrons of the double bond are transferred to the atom other than the one to which the attacking reagent finally gets attached.

Like inductomeric effect, electromeric effect also affects the chemical reactivity of molecules. When both E and I effects operate in opposite directions, the electromeric effect overcomes the inductive effect.

Hyperconjugation

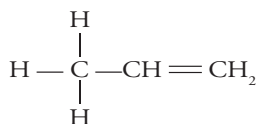
This was given by Baker and Nathan in 1935. It is also known as the **Baker–Nathan Effect**, which takes place in organic molecules in which an alkyl group is attached to the unsaturated system such as multiple bonds or benzene ring.

Baker and Nathan suggested that alkyl groups with at least one hydrogen on the α – carbon atom attached to an unsaturated carbon atom are able to release electrons by a mechanism similar to the electromeric effect, for example

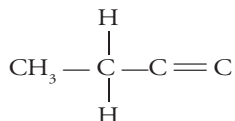


Structures II, III and IV are called the contributing hyperconjugative structures. Hyperconjugation is also termed as *no bond resonance* as there is no real bond between C and one of the hydrogens in these structures.

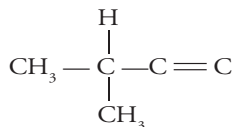
Moreover, greater the number of hydrogen atoms attached to α carbon atom greater will be the electron release by this mechanism.



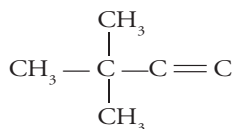
Three hydrogen atoms on the α - carbon atom; hence, three hyperconjugated structures



(2-H on a α carbon atom; hence two hyperconjugated structures)



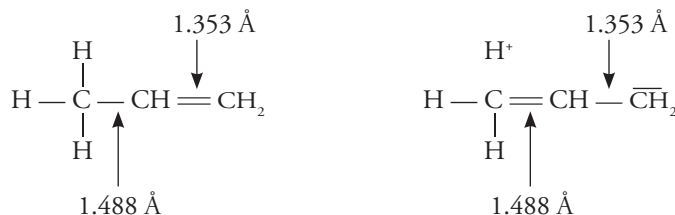
(1-H on a α carbon atom; hence one hyperconjugated structure)



(no hydrogen on α - carbon; hence does not show hyperconjugation)

Effects of hyperconjugation

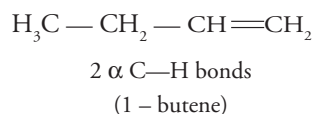
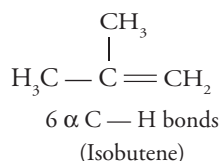
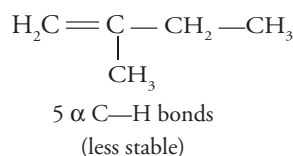
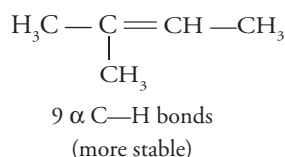
1. **Effect on bond length** The carbon–carbon single bond close to the multiple bond acquires some double bond character. Hence, the bond length reduces.



The C—C bond length is 1.488 Å in contrast to the normal value of 1.54 Å in ethane and the C=C bond length is 1.353 Å as compared to 1.334 Å in ethylene.

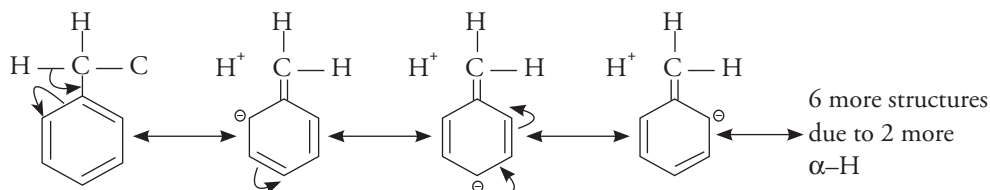
2. **Stability of alkenes** Stability of certain alkenes over others can be explained with the help of hyperconjugation.

For example, 2-methyl-2-butene is more stable than 2-methyl-1-butene as the former has nine α -C—H bonds hence has nine hyperconjugative structures whereas the latter has only five α -C—H bonds and hence only five hyperconjugative structures.

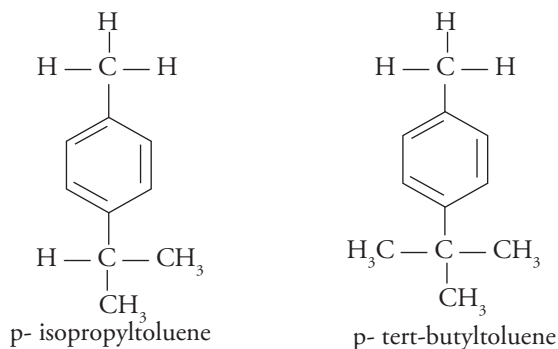


3. **Directive influence of alkyl benzene**

In electrophilic substitution reactions, the methyl group of methyl benzene is *o*, *p* directing. This has been ascribed to +I and hyperconjugative effect.



All the structures show maximum electron density at *o*– and *p*– positions, and hence the electrophilic substitution reaction occurs at the *o*– and *p*– positions.



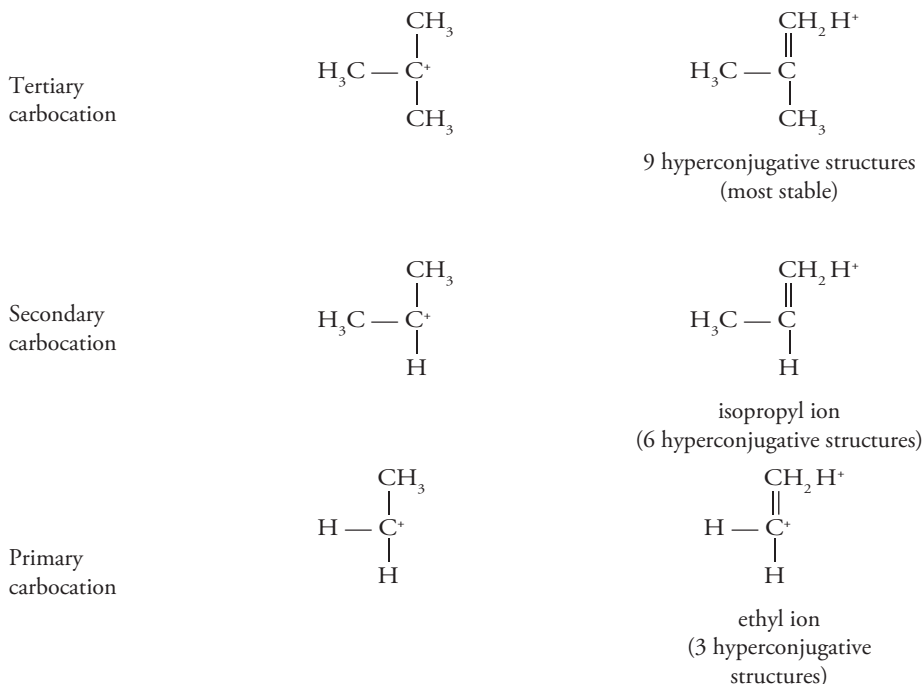
Nitration of p-isopropyltoluene and p-tert butyltoluene yields products with --NO_2 groups attached at position ortho to --CH_3 groups. Hence, in the above cases hyperconjugation effect dominates the +I effect of isopropyl and tert butyl group.

4. Stability of carbocations

The stability of carbocations is in the order

Tertiary > Secondary > primary

The above stability can be explained on the basis of +I effect as well as hyperconjugative effect.



Practice problems

- Give reasons why
 - Methyl amine is more basic than ammonia.
 - Chloroacetic acid is more acidic than acetic acid.
 - Carbon-carbon bond distance in benzene is intermediate between C — C bond distance in ethylene and C — C bond distance in ethanes.
 - CHCl_3 is more acidic than CHF_3 .
 - Formic acid is stronger than acetic acid.
 - Acidic strength decreases in the order.

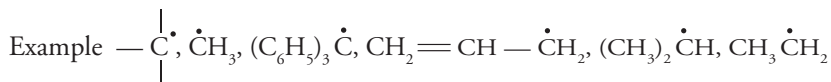
$$\text{CH}_3\text{CH}_2\text{CHClCOOH} > \text{CH}_3\text{CHClCH}_2\text{COOH} > \text{CH}_2\text{ClCH}_2\text{CH}_2\text{COOH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$$
 - Phenol is more acidic than alcohols (ethylalcohol).
- Which among the following undergoes nucleophilic substitution by $\text{S}_{\text{N}}2$ mechanism
 $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $(\text{CH}_3)_2\text{CHBr}$, $(\text{CH}_3)_3\text{CBr}$, CH_3Br
- Aniline is a weaker base than aliphatic amines.

19.5 Reaction Intermediates

As an organic reaction proceeds, homolytic or heterolytic bond cleavage takes place leading to the formation of highly reactive intermediate species. These transient intermediates are known as reaction intermediates. These intermediates have varying stabilities and their half lives range from fraction of a second to several minutes. Their existence has been proved by spectroscopic studies. They may be neutral or charged species, all of them are short lived and very reactive. Some common reaction intermediates are free radicals, carbocations, carbanions, carbenes, nitrenes, benzyne, etc.

The different types of reaction intermediates are discussed below:

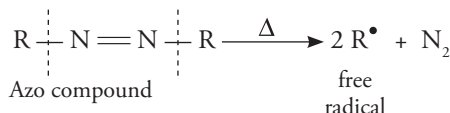
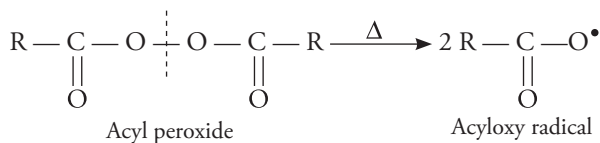
Free radicals A free radical is a neutral species containing an unpaired electron in its valence shell. It shows paramagnetism.



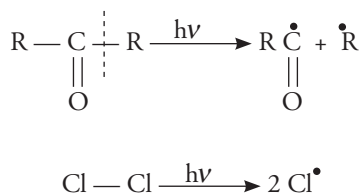
Free radicals are highly reactive species. They have a tendency to pair up and complete their octet.

Generation Free radicals are generally formed in non-polar solvents. They are produced by homolytic cleavage of bonds generally in the presence of high temperature or under the influence high energy radiation.

- **Thermolysis** (bond cleavage at high temperature) of peroxides and azo-compounds produces free radicals.



- **Photolysis** It is the process of formation of free radicals in the presence of sunlight or ultraviolet radiation.



Geometry of free radicals

Free radicals can have both pyramidal (sp^3 hybridised) and planar (sp^2 hybridised) geometries (Fig. 19.1).

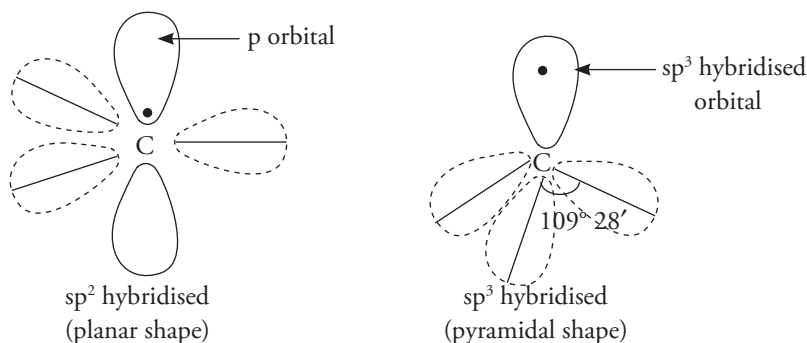


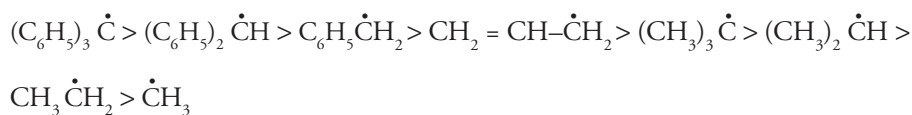
Figure 19.1 Hybridisation and geometry of free radicals

When the free radical is sp^2 hybridised, the three bonds are directed towards the three corners of planar trigonal geometry. The unhybridised p orbital lies perpendicular to the plane and contains the odd electron. For example, $\text{CH}_2=\dot{\text{C}}-\text{CH}_3$ free radical is sp^2 hybridised.

sp^3 hybridised free radical contains the odd electron in the sp^3 hybridised orbital and acquires a pyramidal geometry.

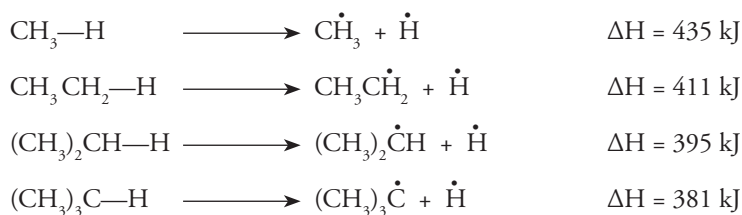
Example $(\text{CH}_3)_3\dot{\text{C}}$, $(\text{C}_6\text{H}_5)_3\dot{\text{C}}$ free radical have pyramidal shape

It has been observed that the stability of free radicals is in the order.

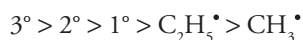


The above order can be explained on the basis of ease of formation, hyperconjugation, resonance and steric factors.

- (i) **Ease of formation** It is easier to break weak bonds. Hence lesser the bond dissociation energy greater is the ease with which the free radical is formed and greater its stability.

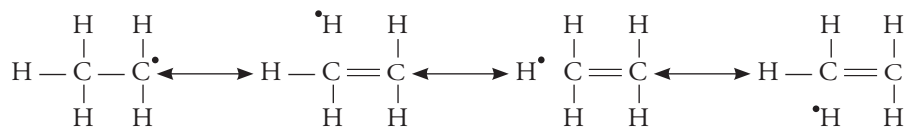


Therefore, the ease of formation of free radicals follows the order.

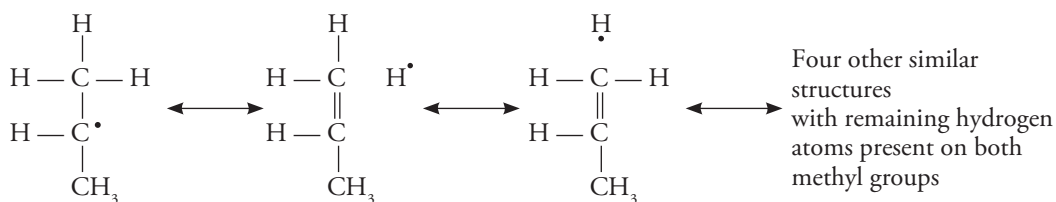


More stable is the radical, the more rapidly it is formed. Hence, the stability of alkyl radicals follows the same order.

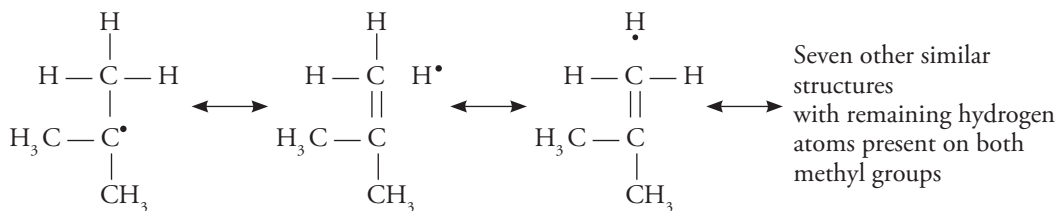
- (b) **Hyperconjugation** The relative stability of 3° , 2° , 1° alkyl radical can be explained on the basis of hyperconjugation. The greater the number of hyperconjugative structures the more stable will be the free radical.



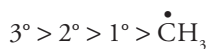
Four canonical structures for primary ethyl free radical.



Seven canonical structures for secondary isopropyl radical.



Ten canonical structures for tertiary butyl radical. Therefore, the order of stability of alkyl free radical is

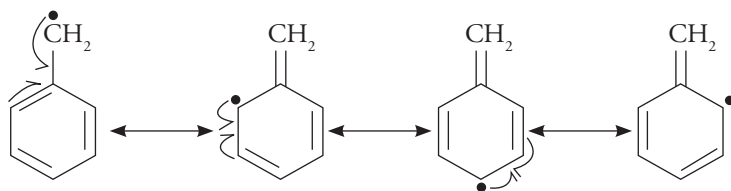


Steric factor also plays a vital role in deciding the stability of free radical. In isobutane there is more steric repulsion hence removal of hydrogen is easier. Moreover, removal of hydrogen relieves the molecule as its bond angle increases from 109° to 120° .

Resonance Allylic and benzylic free radicals are stabilised by resonance; hence, they are more stable than simple alkyl radicals.

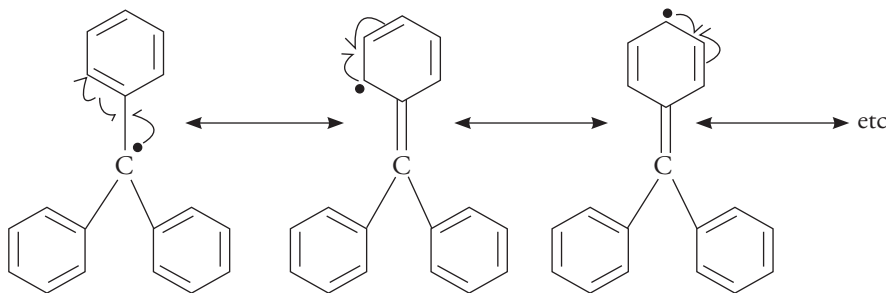


Resonance stabilisation of allyl free radical



Resonance stabilisation of benzyl radical

Diphenylmethyl and triphenylmethyl free radicals are even more stable due to greater resonance stabilisation of these structures.

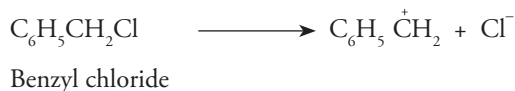
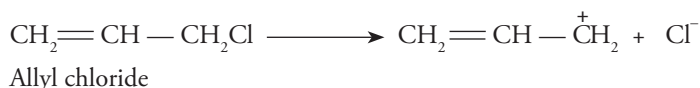


Carbonium ions (carbocations)

The term carbonium ion is widely used in organic chemistry; however, IUPAC recommends the use of the term carbocation and we shall follow the latter. Carbocations is a cation in which the carbon atom bears a positive charge with six electrons in its valence shell. A carbocation is formed due to heterolytic cleavage of the bond in which the leaving group is more electronegative and takes the electron pair with it leaving the carbon electron-deficient.

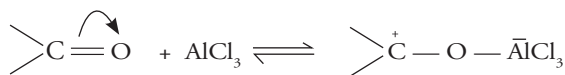
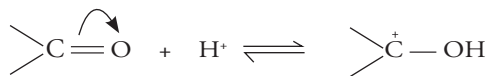
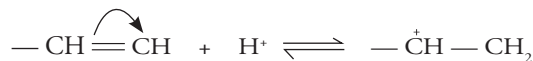
Generation Carbocations can be produced in several ways.

(i) **Direct ionisation** Organic halides form carbocations in the presence of polar medium.

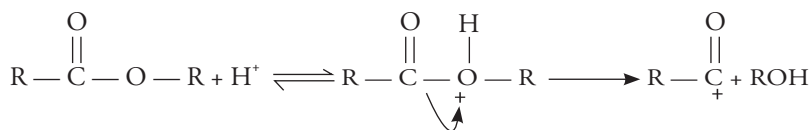
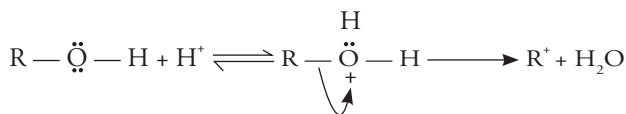


(ii) **Protonation of unsaturated compounds**

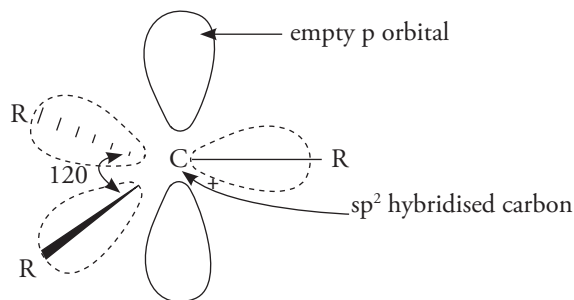
Olefins and carbonyl compounds on being treated with lewis acids or proton-donating solvents yield carbocations.



(iii) **Protonation of atoms having lone pair of electrons**

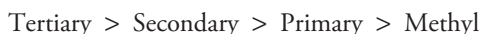
**Geometry of carbocations**

The central carbon atom of the carbocations is sp^2 hybridised. The three bonds attached to it are planar and the bond angles are 120° . The unhybridised p orbital lying perpendicular to the plane of hybridised orbitals is empty Figure 19.2.

**Figure 19.2** Geometry of carbocation

Stability of carbocation Greater the dispersal of positive charge greater is the stability of the carbocation. If the charge is localised, then the stability of the carbocation will decrease.

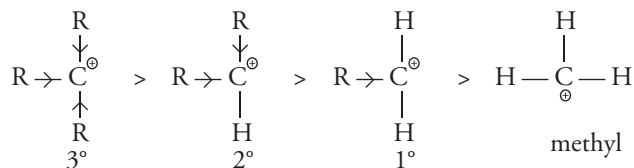
Stability of simple carbocation is as follows:



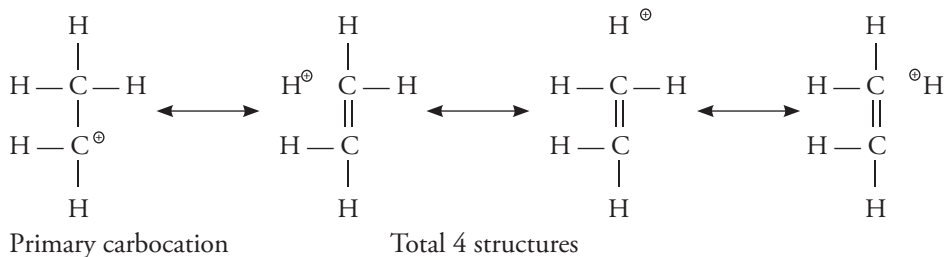
The above order of stability can be explained by two factors: inductive effect and hyperconjugation.

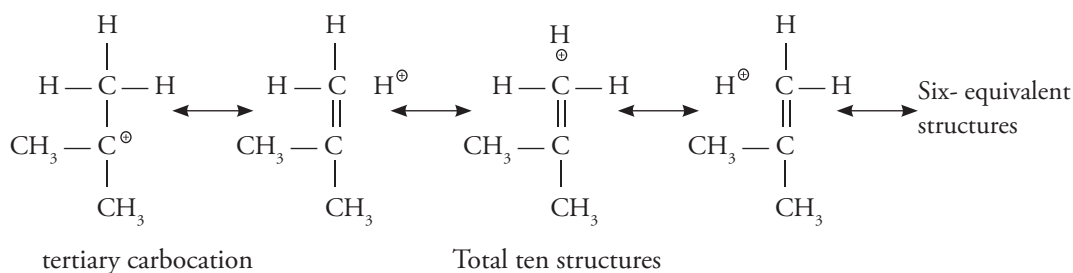
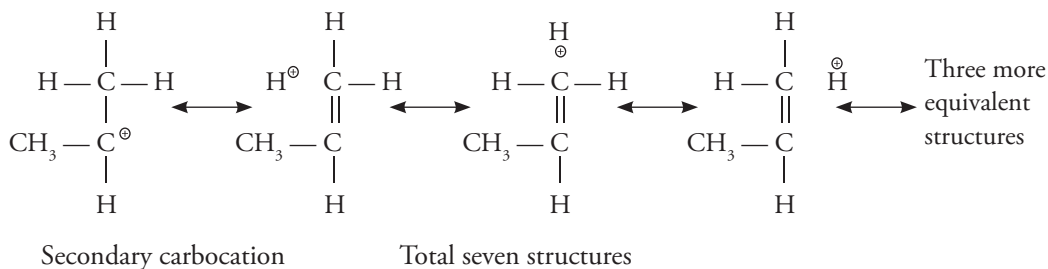
- (a) **Inductive effect** As we know that the alkyl groups have + I inductive effect, that is, electron releasing effect. The alkyl groups attached to the positively charged carbon atom tend to release electrons towards carbon. As a result, the positive charge on the carbon atom decreases but the alkyl group becomes somewhat positive. As a result, the positive charge on the carbon atom gets dispersed. The dispersal of charge leads to increased stability. Therefore, more the alkyl groups, greater will be the charge dispersal and more stable will be the carbocation.

Thus, tertiary carbocations with three alkyl groups attached to positive carbon is more stable than secondary carbocation with two alkyl groups which in turn is more stable than primary carbocation. The primary carbocation is more stable than the methyl carbocation with no charge dispersal.

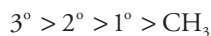


- (b) **Hyperconjugation** The greater stability of alkyl substituted carbocations can be partly attributed to the phenomenon of hyperconjugation in which there is delocalisation of σ electrons.

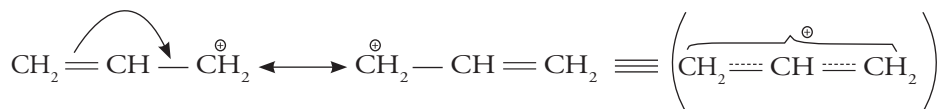




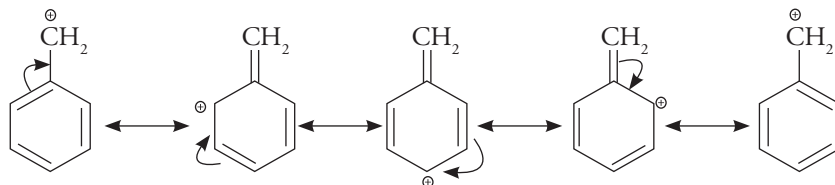
Tertiary carbocation has ten, secondary has seven and primary has four hyperconjugative structures. Greater the number hyperconjugative structures, greater is the stability. Hence, the order stability is



(c) **Resonance** Stability of benzyl and allyl carbocations is explained on the basis of resonance.

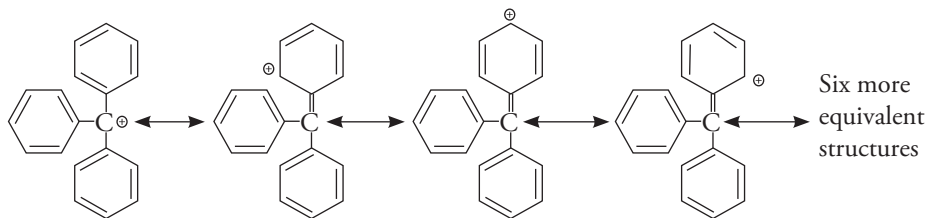


Resonance stabilisation of allyl cation

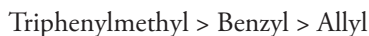


Resonance stabilisation of benzyl cation

The triphenylmethyl carbocation is extremely stable. It is regarded as the most stable carbocation. Its remarkable stability is due to extensive dispersal of positive charge as shown below.

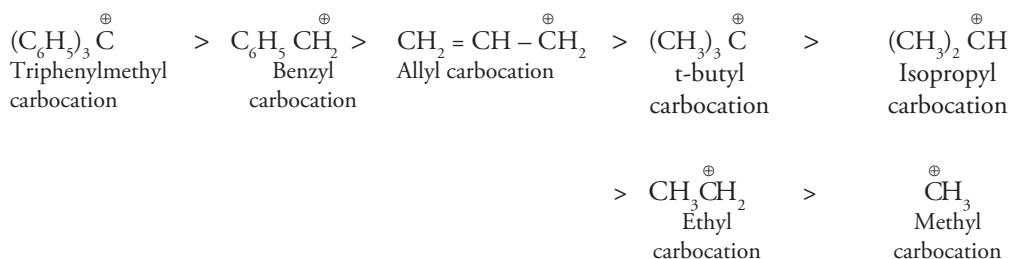


The order of stability is



These carbocations are more stable than the alkyl carbocations.

The overall order of stability of the carbocations is



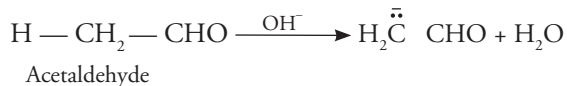
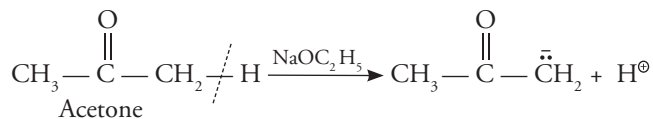
Carbanions A carbanion is defined as an organic species containing negatively charged carbon atom. The carbon atom in a carbanion is trivalent and has two extra electrons which are not bonded.

Generation

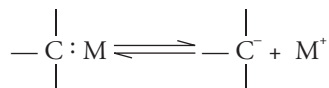
- (i) A carbanion is formed by the heterolytic fission of a bond attached to the carbon atom in such a way that the carbon retains the electron pair. Hence, carbon acquires a negative charge.

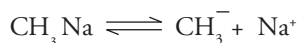
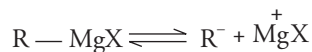


The reaction generally occurs in the presence of a base.

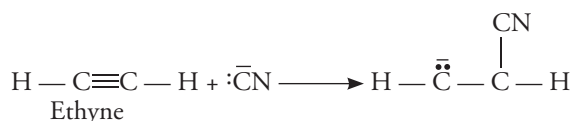
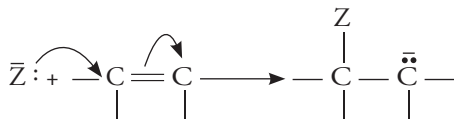


- (ii) Carbanions can also be formed by breaking of carbon metal bonds of organometallic compounds





(iii) By nucleophilic attack on a carbon–carbon multiple bond



Structure of carbanion

The carbon atom of the carbanion is sp^3 hybridised. Three of the four sp^3 hybrid orbitals form sigma bonds with the other groups whereas the fourth sp^3 hybrid orbital contains the lone pair of electrons. Hence, it has a pyramidal shape similar to that of ammonia (Fig. 19.3).

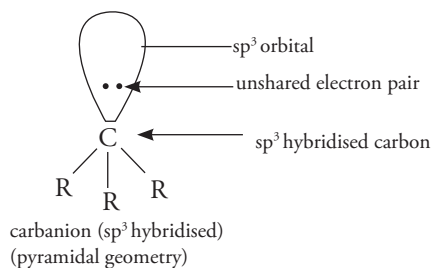
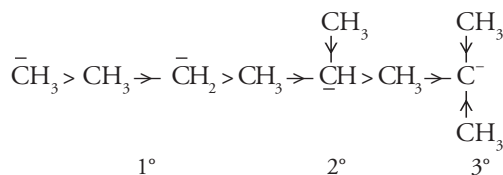


Figure 19.3 Geometry of carbanion

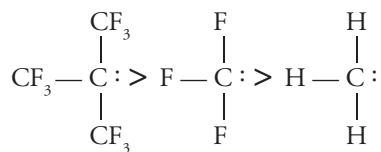
Stability of carbanion

(i) Presence of electron releasing groups (+I effect) intensifies the negative charge on the carbon making the anion less stable. Greater the number of alkyl groups, greater will be the negative charge density at the central atom and less will be the stability of the carbanion.

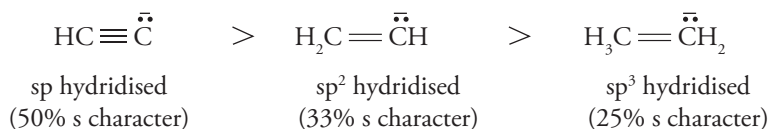


$\bar{C}H_3$ is the most stable followed by primary, secondary and tertiary carbanion.

If electron withdrawing groups (–I effect) are introduced the stability of the carbanion greatly increases.

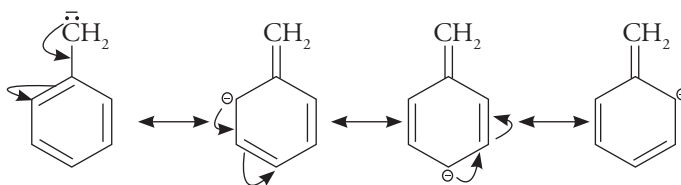


- (ii) **s-character** Greater the s-character of the carbon atom having negative charge, greater will be its stability.



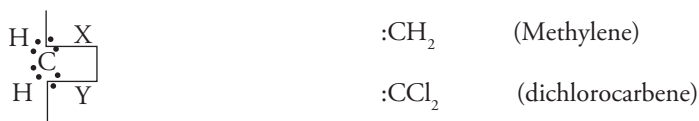
Higher the s character, closer are the electrons to the nucleus and more is the stability.

- (iii) **Resonance** The carbanion is stabilised by resonance due to delocalisation of the negative charge which is distributed over other carbon atoms in the resonating structures. For example:

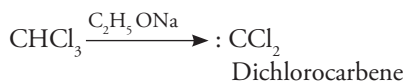
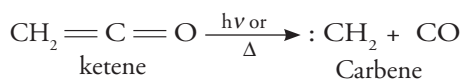


Carbenes

It is a short lived, neutral, divalent carbon with two unpaired electrons. It has six electrons in its valence shell and is formed by homolytic fission:



The simplest carbene is methylene which is generated by the decomposition of diazomethane:



Structure of carbene

Methylene can exist in two forms—singlet and triplet. In singlet state the two non-bonded electrons are in the same orbital and paired and it is sp^2 hybridised (Fig. 19.4 a). Triplet methylene (carbene) is sp of sp^2 hybridised. sp hybridised methylene has two electrons are placed in p_y and p_z orbital and it is linear (Fig. 19.4 b) whereas sp^2 hybridised methylene is bent (bond angle 140° – 150°).

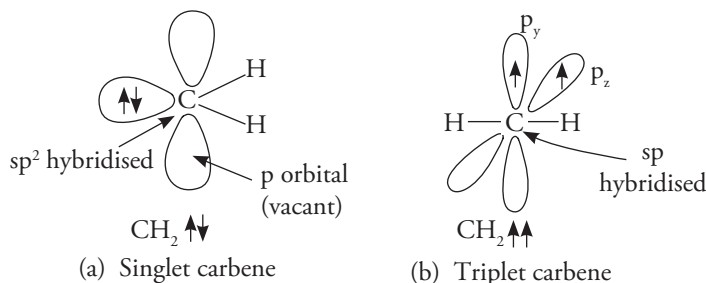


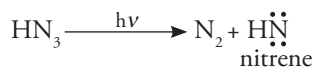
Figure 19.4 Structure of carbenes

Nitrenes

Nitrenes are intermediate species containing nitrogen atom having one bond pair and two lone pairs. It is an electron-deficient nitrogen and is analogous to carbenes.



It is also called imidogen, azene or imene. They can be present in both singlet and triplet states and can be generated by the hydrolysis of hydrazoic acid in aromatic solvents.



Hofmanns rearrangement reaction occurs by the formation of intermediate nitrene (refer to Section 19.10).

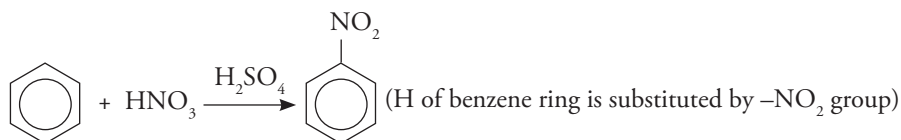
19.6 Types of Organic Reactions

Organic reactions are broadly classified as

- (i) Substitution reactions
- (ii) Addition reactions
- (iii) Elimination reactions
- (iv) Rearrangement reactions

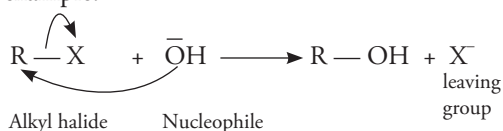
Let us discuss these reactions one by one.

Substitution Reactions A substitution reaction is one in which an atom or group of atoms in a molecule is replaced or substituted by different atom or group of atoms. They can also be termed as displacement reactions. For example:



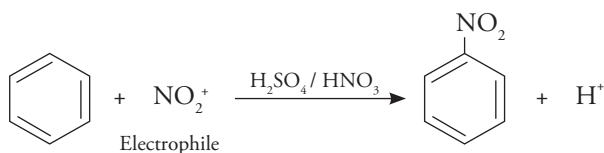
The attacking species in substitution reactions can be nucleophile, electrophile or a free radical. Depending on the nature of the attacking species the substitution reactions are of three types.

- (a) **Nucleophilic Substitution Reactions** Reactions in which substitutions are brought about by nucleophiles are called nucleophilic substitution reactions. They are denoted by S_N (S = substitution, N = nucleophilic). These reactions are characteristic of alkyl halides. For example:



The mechanism of nucleophilic substitution is discussed later in Section 19.7.

- (b) **Electrophilic Substitution Reactions** These reactions are characteristic of aromatic compounds like benzene and are brought about by electrophiles which attack the high electron density of the aromatic system. For example, nitration of benzene ring.



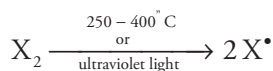
The detailed mechanism is discussed in Section 19.8.

- (c) **Free Radical Substitutions Reactions** In this type of reactions, the substitution is brought about by free radicals. Example: Halogenation of alkanes in the presence of sunlight.



The reaction occurs in three steps:

- (i) **Initiation** Free radicals are generated in this step. Halogens in the presence of sunlight form free radicals.

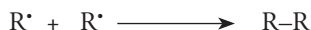
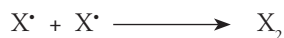


(ii) **Propagation** The free radicals formed in the initiation step attack the alkane.



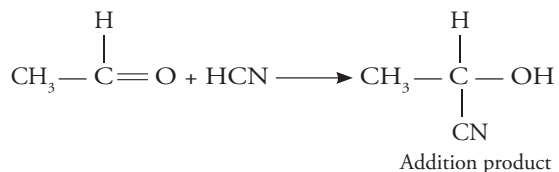
The reaction continues till finally the chain is terminated.

(iii) **Termination** The free radicals combine to terminate the chain. The following reactions can occur.



Addition Reactions An addition reaction is one in which the attacking reagent adds up to the reactant molecule to form a single product. Addition reactions occur in compounds containing double or triple bonds.

For example



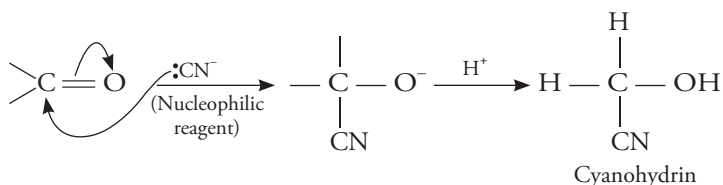
Like substitution reactions, addition reactions can also be nucleophilic, electrophilic or free radical addition reactions depending on the type of attacking reagent.

(a) **Nucleophilic Addition Reactions** Addition reactions which are brought about by nucleophiles are called nucleophilic addition reactions. Common examples of compounds undergoing nucleophilic addition reactions are aldehydes, ketones, esters, etc.

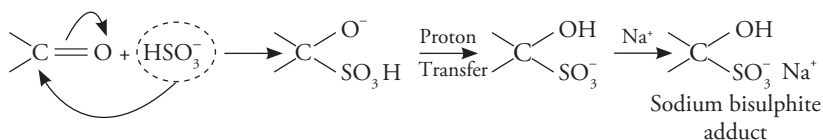
In aldehydes, ketones and esters, the π electrons are pulled towards oxygen (as it is more electronegative than carbon) making the carbonyl carbon electron-deficient and the carbonyl oxygen electron-rich.



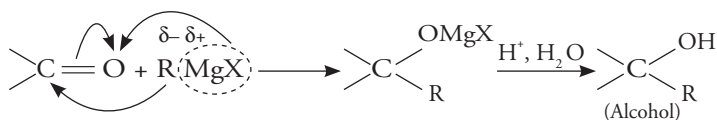
The nucleophile uses its electron pair and forms a bond with the carbon atom of carbonyl group. The electrophile then associates itself with the oxygen atom and the final addition product is formed. The above mechanism can be explained by considering the addition of HCN to a ketone to form cyanohydrin. In the addition reaction the strongly basic cyanide ion attacks the carbonyl carbon; subsequently (or possibly simultaneously) the oxygen accepts hydrogen ion to form the cyanohydrin product.



Similarly, addition of sodium bisulphite takes place as follows:

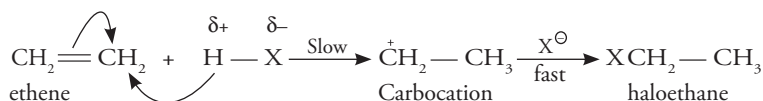


Consider the addition of Grignards reagents:



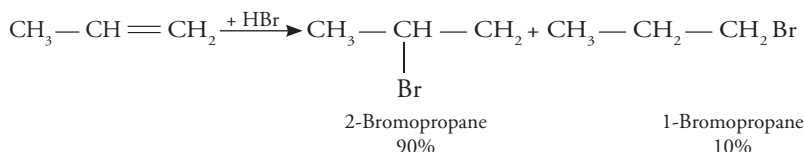
- (b) **Electrophilic Addition Reactions** Addition reactions brought about by electrophiles are called electrophilic addition reactions. They are characteristic of alkenes, alkynes and occur by the formation carbocations as intermediates.

Consider the addition of hydrogen halides to alkenes:

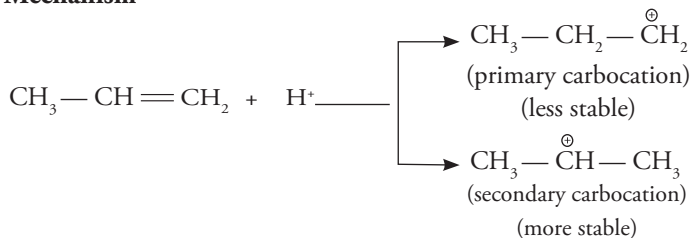


Electrophilic addition to asymmetrical alkenes takes place in accordance to the 'Markownikoffs rule'.

According to this rule, *during addition across unsymmetrical double bond, the negative part of the attacking reagent attaches itself to the carbon atom carrying lesser number of hydrogen atoms while positive part goes to the carbon atom with more number of hydrogen atoms.*



Mechanism



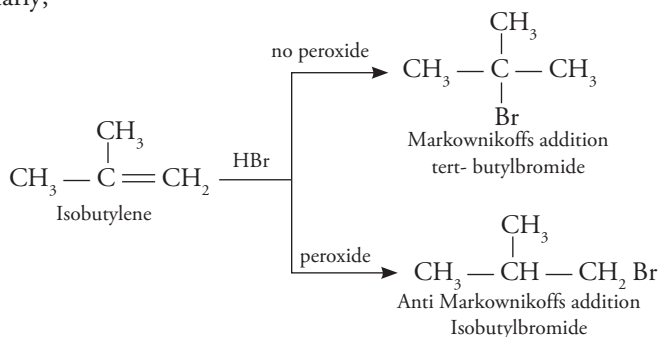
The free radical formed above is attacked by HBr to form the product. Since secondary free radical is more stable than primary free radical, hence the final product is obtained from the secondary free radical.



Chain termination



Similarly,

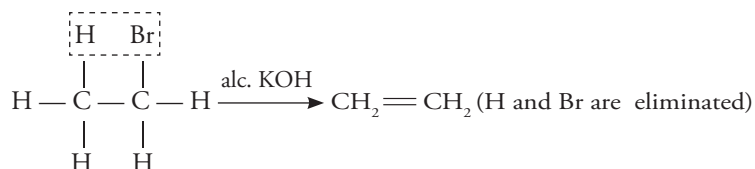


Elimination Reactions

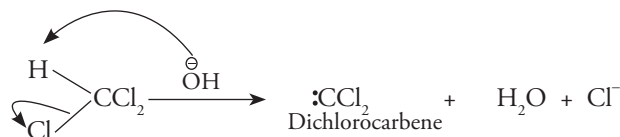
The term 'eliminate' means 'to remove'. Elimination reactions are those reactions in which a molecule loses atoms or groups without being replaced by other atom or group. These reactions are of two types.

- (i) **β - Elimination** If the two atoms or groups are lost from the vicinal (adjacent) carbon atoms, it is called β -elimination. β -elimination leads to the formation of double and triple bonds

For example:



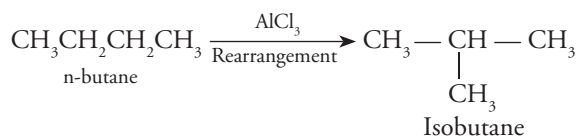
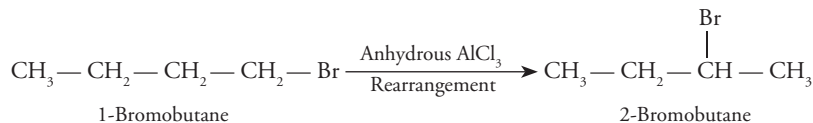
- (ii) **α -Elimination** If the two atoms or groups are lost from the same carbon atom, it is called an α -elimination or 1, 1 elimination. The most common example of α -elimination reaction is the generation of dichlorocarbene from chloroform in the presence of a base.



The carbene thus formed is unstable and reacts quickly to form products.

β - elimination reactions are more common than α -elimination reactions. Brief mechanism of elimination reactions is discussed in Section 19.9.

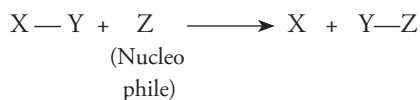
Rearrangement Reactions These reactions involve the migration of an atom or group of atoms to another position within the molecule under suitable conditions. For example:



Beckmann's rearrangement (discussed in Section 19.10)

19.7 Mechanism of Nucleophilic Substitution Reactions

These reactions constitute the most important class of organic reactions and involve the substitution or replacement of one group or atom by the other to form a new compound.



In the above example, the atom X is replaced by Z to form the new product. Nucleophilic substitution reactions are represented as S_{N} reactions. The carbon compound on which the substitution occurs is called the substrate. The group which is replaced by the attacking reagent (nucleophile) is called the leaving group. The leaving group leaves the substrate carrying its electron pair with it.

Substitution reaction involves:

- Bond breaking to release the leaving group
- Bond formation with the nucleophile

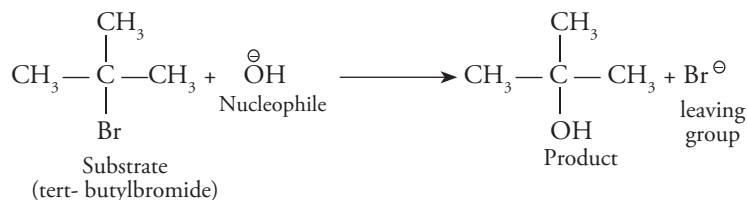
Two types of mechanisms have been proposed for substitution reaction.

- (i) $\text{S}_{\text{N}}1$ Mechanism (Substitution nucleophilic unimolecular)
- (ii) $\text{S}_{\text{N}}2$ Mechanism (Substitution nucleophilic bimolecular)

$\text{S}_{\text{N}}1$ Mechanism (Substitution Nucleophilic Unimolecular)

This type of substitution reaction takes place in two steps through the formation of intermediate carbocation.

Consider the example

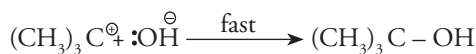


The above reaction is considered to be taking place in two steps

- (i) The first step is slow and reversible. It involves the ionisation of C–Br bond to form a carbocation, $(\text{CH}_3)_3\text{C}^+$ and a bromide ion Br^- .



- (ii) The second step is fast and involves the reaction of the carbocation and hydroxyl ion (nucleophile) to yield an alcohol.

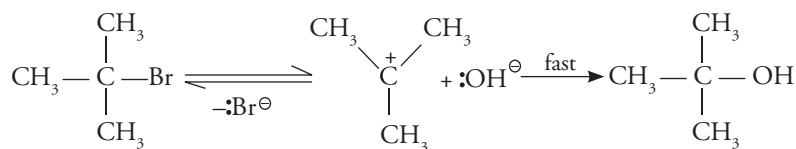


As the rate of a reaction is determined by the slow step (called rate determining step), the rate law expression for the above reaction can be written as

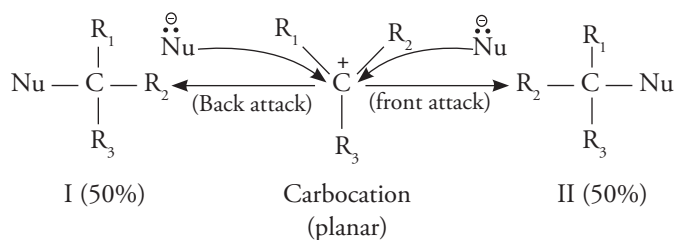
$$\text{Rate} = k [(\text{CH}_3)_3\text{C} - \text{Br}]$$

Hence the reaction follows first order kinetics and since only one molecule takes part in the rate determining step it is termed as unimolecular.

The carbon atom in the carbocation is sp^2 hybridised, it is planar and the overall reaction can be written as



Stereochemistry of $\text{S}_{\text{N}}1$ Reaction As discussed above, the intermediate carbocation formed in $\text{S}_{\text{N}}1$ mechanism is sp^2 hybridised and is planar. Hence the nucleophile can attack from either face of the cation. Hence, if the carbocation has been derived from an asymmetric (optically active) alkyl halide, then the product will be a racemic mixture.



Structures I and II are enantiomers.

Energy Changes in S_N1 Reaction The energy changes occurring during an S_N1 reaction can be represented by an energy profile diagram (Fig. 19.5). Every step of the S_N1 reaction has its transition state.

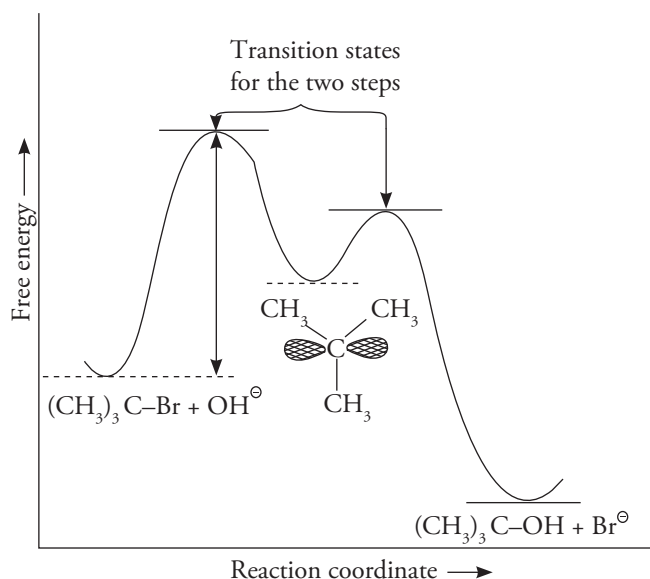
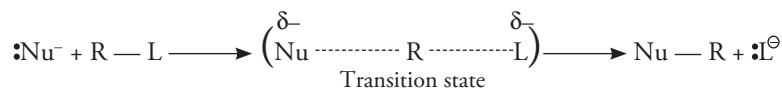
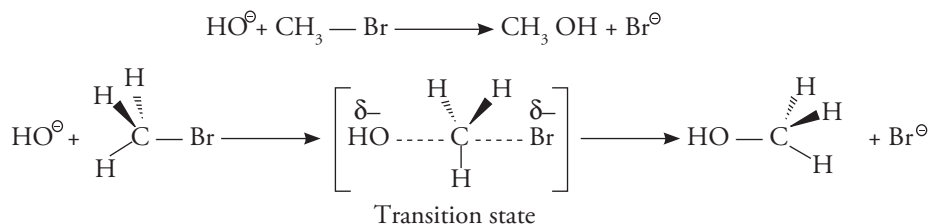


Figure 19.5 Energy changes in S_N1 reaction

S_N2 Mechanism (Substitution Nucleophilic Bimolecular) This type of substitution reaction takes place in a single step. In this mechanism, bond making and bond breaking take place simultaneously and there is direct displacement of the leaving group with the attacking nucleophile.



Consider the reaction of methylbromide with sodium hydroxide to yield methanol.

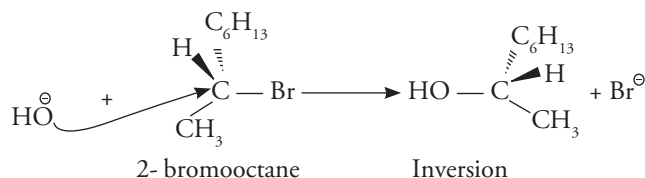


The rate of the reaction depends on the concentration of both the reactants.

$$\text{Rate} = k [\text{CH}_3\text{Br}] [\text{OH}^-]$$

Since both the reactants take part in the rate determining step, it is a bimolecular reaction and the mechanism is called $\text{S}_\text{N}2$ mechanism (Ingold).

Stereochemistry of $\text{S}_\text{N}2$ Mechanism In the $\text{S}_\text{N}2$ mechanism, the nucleophile attacks the side of the carbon atom opposite to that of the leaving group. Hence, in $\text{S}_\text{N}2$ mechanism the stereochemistry of the product is opposite to that of the substrate. In other words $\text{S}_\text{N}2$ mechanism proceeds with stereochemical inversion, commonly referred to as Walden inversion. It can be illustrated by the hydrolysis of asymmetric halide 2-bromooctane.



Energy Changes in $\text{S}_\text{N}2$ Mechanism The energy changes can be described by the energy profile diagram as shown in Figure 19.6.

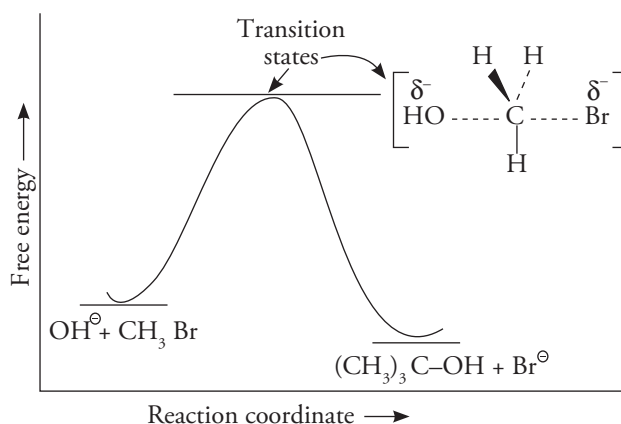
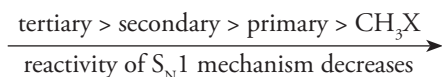


Figure 19.6 Energy profile diagram for $\text{S}_\text{N}2$ reactions

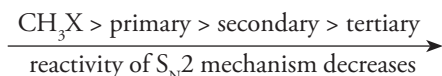
Factors Affecting the Reactivity and Mechanism of Nucleophilic Substitution Reactions

A nucleophilic substitution reaction can proceed by S_N1 or S_N2 mechanism. Which mechanism is to be followed depends upon various factors. The reactivity and rate of reaction is also influenced by several factors like nature of substrate, nature of solvent, nature of nucleophile, nature of leaving group, etc. Let us discuss these factors one by one.

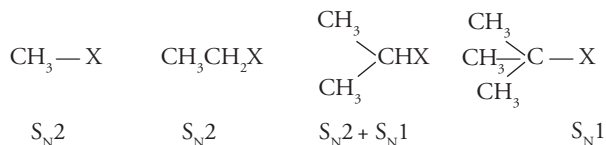
- Nature of substrate** S_N1 reactions proceed by the formation of intermediate carbocation whereas in S_N2 reactions the nucleophile attacks from the rear end and the transition state having partially bonded leaving group and partially bonded attacking reagent (nucleophile) is formed. Factors like inductive effect, hyperconjugation and resonance which stabilise the intermediate carbocation favor S_N1 reactions whereas steric factors which assist or hinder the bond formation of nucleophile and bond cleavage of leaving group will play a decisive role in determining the reactivity of S_N2 mechanism. The sequence of reactivity of alkyl halides to S_N1 reactions is in the following order:



The reactivity of alkyl halides to S_N2 reactions is in the following sequence:

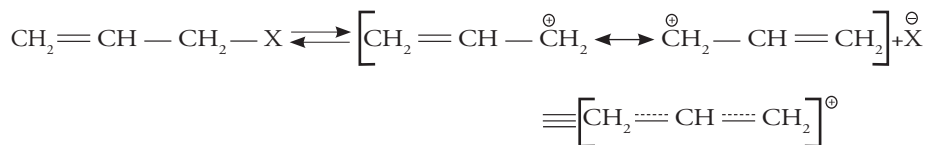


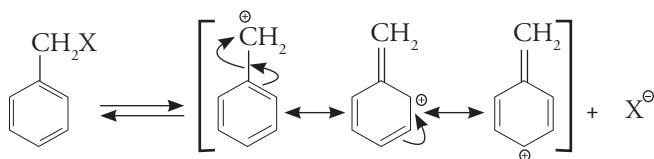
It can be seen from the above order that tertiary alkyl halides are substituted by S_N1 mechanism whereas the primary alkyl halides follow S_N2 substitution reactions. Secondary alkyl halides can undergo substitution by both S_N1 and S_N2 mechanisms:



We can see that the introduction of methyl groups changes the mechanism from S_N2 to S_N1 . This change in mechanism can be explained by the following factors.

- Inductive, hyperconjugation effects** S_N1 reactions proceed by the formation of carbocations. + I effect of methyl groups and hyperconjugation stabilise the carbocations (Refer to Section 19.4 inductive effect and hyperconjugation). This effect is maximum in tertiary carbocations, and hence they react exclusively by S_N1 mechanism.
- Resonance effect** Allylic and benzylic substrates readily undergo S_N1 reaction because the intermediate carbocation is resonance-stabilised.

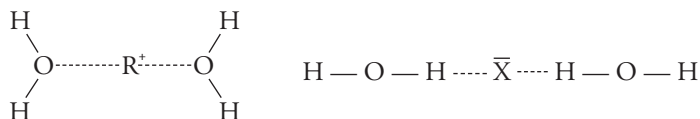




(iii) **Steric hindrance** In S_N2 mechanism, the nucleophile attacks from the backside on the alkyl halides leading to a transition state. In primary halides it is easier for the nucleophile to push itself between the hydrogen atoms, and hence primary halides undergo substitution by S_N2 mechanism. As the hydrogen atoms are replaced by alkyl groups, the nucleophile finds it difficult to approach the carbon site. Hence, S_N2 mechanism becomes difficult in secondary alkyl halides and tertiary alkyl halides react exclusively by S_N1 mechanism.

2. Nature of solvents As S_N1 reactions proceed by the initial ionisation of the molecule producing carbocation hence polar solvents are found to increase the rate of S_N1 reaction because

- (i) They facilitate the ionisation of the molecule.
- (ii) They stabilise the liberated ions by solvation.



The cations are solvated by the solvent molecules through coordination with electron pair, whereas the anions are solvated by solvent molecules through hydrogen bonding.

The above observation is supported by experimental results. The rate of hydrolysis of *t*-butylchloride in 50% aqueous ethanol is 30,000 times faster than 100% ethanol.

On the contrary the rate of S_N2 mechanism does not alter appreciably with the solvent.

3. Effect of nucleophile

S_N1 Reactions

Rate \propto [Substrate]

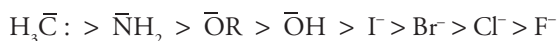
The rate equation shows that nucleophilic reagent does not take part in the rate-determining step. Hence, the entering group has no effect on the rate of S_N1 reactions.

S_N2 Reaction

Rate \propto [Substrate] [Nucleophile]

The rate of reaction depends on the nature of the nucleophile. The more strongly nucleophilic the reagent, that is, the greater the tendency of the reagent to donate electrons to the substrate molecule, the faster will be the reaction.

The decreasing order of basicity of few nucleophiles is given below:



The rate of reaction also decreases in the above order.

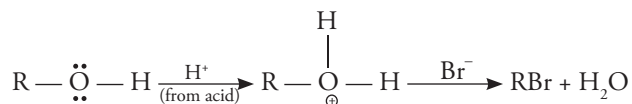
4. Nature of leaving group The less basic the leaving group, the more easily it is displaced by the solvent in S_N1 mechanism or by the attacking nucleophile in S_N2 reactions.

In alkyl halides, the ease of separation of halide ions is $I^- > Br^- > Cl^- > F^-$. This is the reverse of carbon halogen bond strength. The easily the leaving group is polarised the more reactive is the alkyl halide.

Here it is important to note that both the entering and leaving groups are bases. Hence strong nucleophilic reagents will displace the weaker base. For example, alkaline hydrolysis of alkyl halide.



If it is the reverse, that is, if the leaving group is more basic than the entering group then it will not be displaced in ordinary conditions but can be made to do so in acid solution which makes them less basic due to protonation. For example, conversion of alcohols to alkyl halides.



This is the reason why alcohols undergo substitution reactions in acidic conditions only.

Table 19.2 Comparison between S_N1 and S_N2 reaction

	S_N1	S_N2
1	They show first order kinetics	They follow second order kinetics. In the presence of excess of nucleophile they may follow first order kinetics, but still the reaction proceeds by S_N2 mechanism
2	Rate of reaction is mainly affected by electronic factors	Rate of reaction is determined by steric factors
3	Rearranged products can be formed. The intermediate carbocation formed can rearrange to form stable carbocations	Since carbocations are not formed rearrangement is not possible
4	Reactivities of halide $t > s > p > \text{methyl}$	Reactivities of halides $CH_3 > p > s > t$
5	Favoured by mild nucleophiles	Favoured by strong nucleophiles
6	Favoured by low concentration of nucleophiles	High concentration of nucleophiles is needed
7	Favoured by solvents of high polarity	Favoured by solvents of low polarity
8	Stereochemistry-partial racemization of products occurs	Complete inversion of products occurs

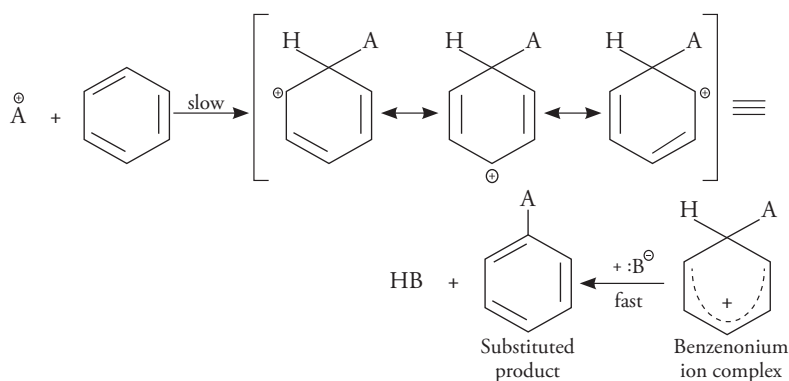
19.8 Mechanism of Electrophilic Substitution Reactions

As discussed in Section 19.6, reactions which are brought about by electrophiles are called electrophilic substitution reactions. These reactions are characteristic of aromatic compounds.

Although aromatic compounds have double bonds but they do not undergo addition reactions under normal conditions. The lack of reactivity to addition reactions is due to the greater stability of aromatic ring systems due to complete π electron delocalisation (resonance). The aromatic compounds react by electrophilic aromatic substitution reactions in which the aromaticity of the ring system is preserved.

Mechanism Electrophilic substitution reaction involves attack by an electrophile and liberation of a proton. This takes place in two steps:

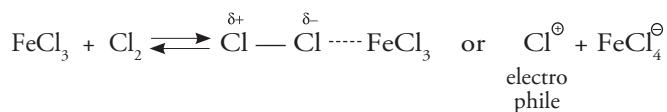
- In the first step the electrophile attacks the benzene ring to form an intermediate carbocation called the benzenonium ion. This step is slow and is the rate determining step.
- In the second step, which is fast, a proton is removed from this intermediate yielding the substituted product.



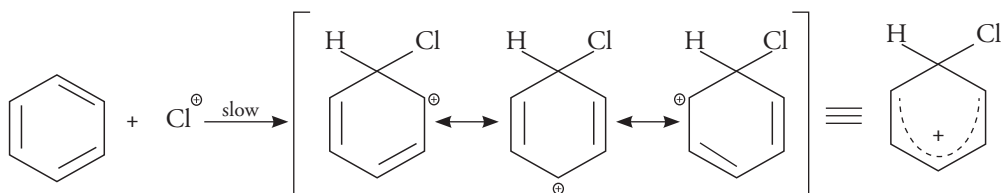
Some typical electrophilic substitution reactions of benzene are discussed below:

Halogenation

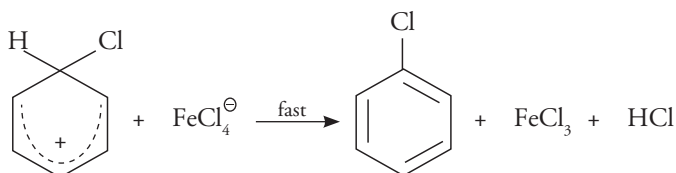
Halogenation is carried in the presence of a catalyst which acts as a halogen carrier. The commonly used catalysts are iron powder, $FeCl_3$, $ZnCl_2$, $AlBr_3$, iodine, pyridine, etc. The main function of the halogen carrier is to polarise the halogen–halogen bond and generate the electrophile.



The electrophile then attacks the aromatic ring.



Finally the aromatic structure is restored by loss of proton to FeCl_4^- and the catalyst is regenerated.



Nitration

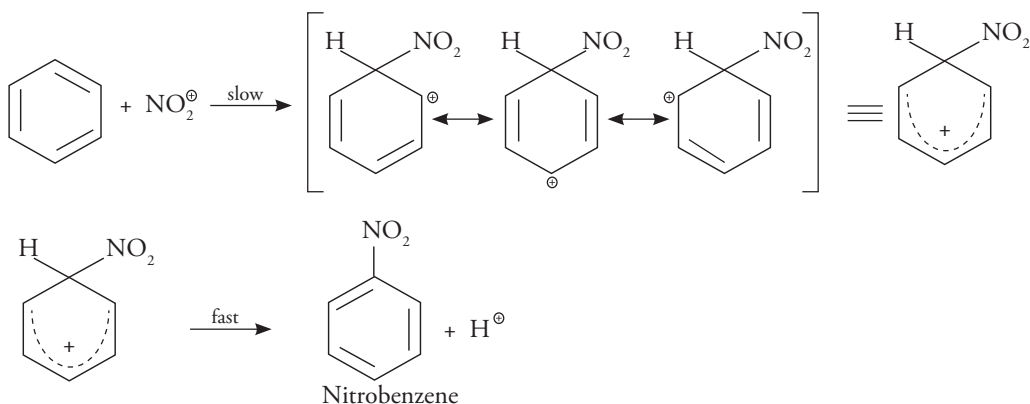
Nitration is brought about by treating benzene with a mixture of concentrated nitric acid and sulphuric acid. Nitronium ion (NO_2^+), which brings about the nitration, is generated in situ.



Nitronium ion can also be generated using BF_3 and HF as catalysts.

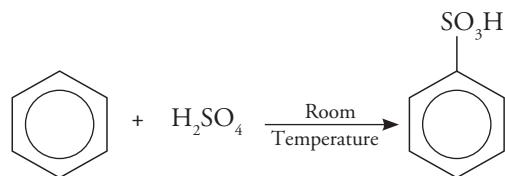


The nitronium ion thus produced attacks the benzene ring followed by the loss of proton to form nitrobenzene.

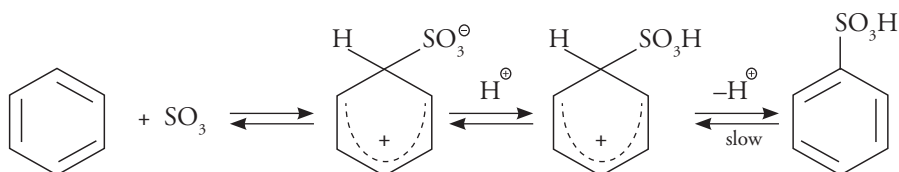


Sulphonation

Benzene reacts with concentrated sulphuric acid at room temperature to produce benzene sulphonic acid.



The electrophile involved is sulphur trioxide.

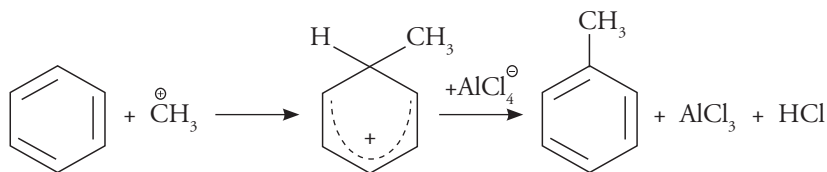


Here, it is important to note that the second step, removal of proton, is the rate-determining step.

Friedel Craft Alkylation

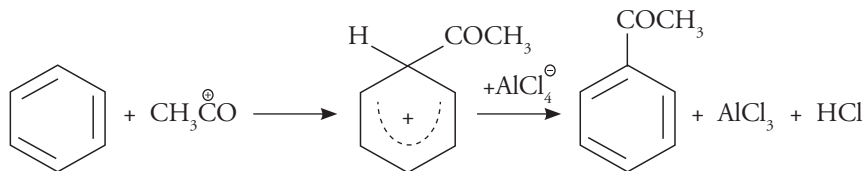
Benzene reacts with alkyl halides in the presence of a lewis acid (generally AlCl_3) to produce alkylated products. Other lewis acids like BF_3 , AlBr_3 , etc. can also be used.

The lewis acid assists in the generation of electrophile which attacks the benzene ring followed by abstraction of proton.



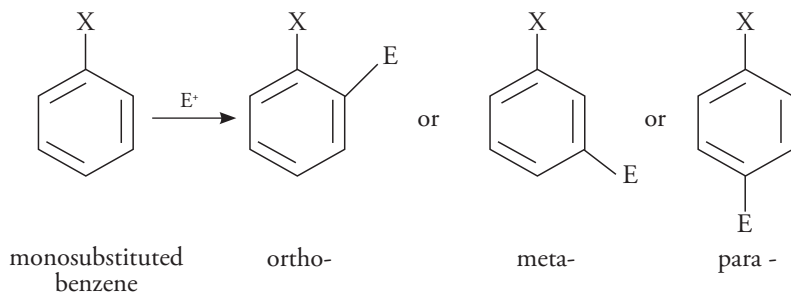
Friedel Craft Acylation

In friedel craft acylation, the acylating species is produced by the reaction of acid halides or anhydrides with a lewis acid.



Effects of Substituents

When benzene undergoes electrophilic substitution, initially a monosubstituted product is formed because all the six carbon atoms are the same. However, if a monosubstituted benzene further undergoes electrophilic substitution the new group can enter at ortho, meta or para position with respect to the group already present on the benzene ring.



The substituent X exerts two types of effects on the benzene ring for further substitution.

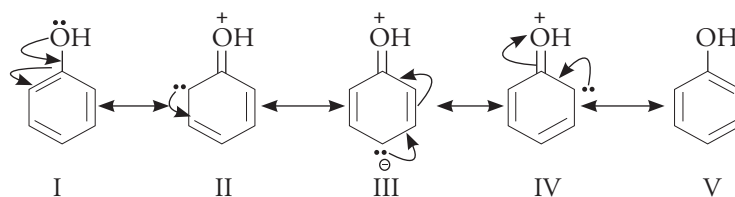
- (i) **Directive influence** The substituent X may direct the incoming group to *o*, *m* and *p* position depending on the nature of the substituent. The effect is also called the orientation effect.
- (ii) **Activity effect** The group already present may activate or deactivate the benzene ring towards further substitution.

On the basis these characteristics the substituents are divided into three categories.

- 1 Groups such as alkyl, OH, NH₂, NR₂, NHCOR, OR and OCOR are *o*, *p* directing and activate the benzene ring for further substitution.
- 2 Halogens which although *o*, *p* directing exert a deactivating effect on the benzene ring.
- 3 Groups such as –C = O, –C ≡ N, SO₂, –NO₂ – $\overset{+}{N}R_3$ are *m* directing and deactivate the benzene ring.

Activating Groups : Ortho – Para Directors

All ortho and para directing groups have a lone pair of electrons except the methyl group. They donate the lone pair of electrons to benzene ring due to resonance and increase the electron density at *o*- and *p*- positions. Hence the substitution occurs at *o*- and *p*- positions.



It is clear from structures II, III and IV that the electron density at *o*- and *p*- position is high; hence, electrophilic substitution occurs at these positions.

On the other hand –OH groups also exerts –I effects (electron withdrawing effect); but the resonance effect is much powerful than the –I effect.

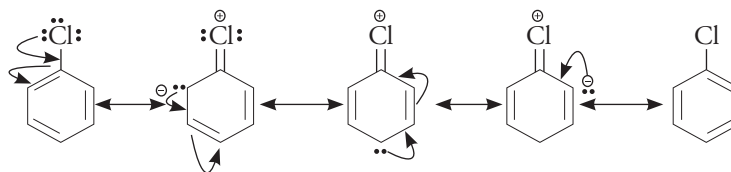
Effect of alkyl groups

Alkyl groups do not have a lone pair of electrons, and hence do not undergo mesomeric (resonance) effect. However, they have strong +I effect which increases the electron density at *o*- and *p*-position, directing the incoming groups to these position.

Deactivating groups: ortho-para directors

Halogens are *o*- and *p*- directing but deactivating. The lone pair of electron conjugates with the benzene ring and increases the electron density at *o*- and *p*- position (resonance effect), and directs the incoming group to ortho and para position. But on the other hand halogens exert a strong $-I$ effect, which tends to remove electrons from ortho and para positions.

So the net result is that although halogen atoms are *o*, *p* directing due of +R effect, they deactivate the ring due to $-I$ effect ($+R \geq -I$) and hence compared to benzene it is difficult to carry out the substitution in chlorobenzene.



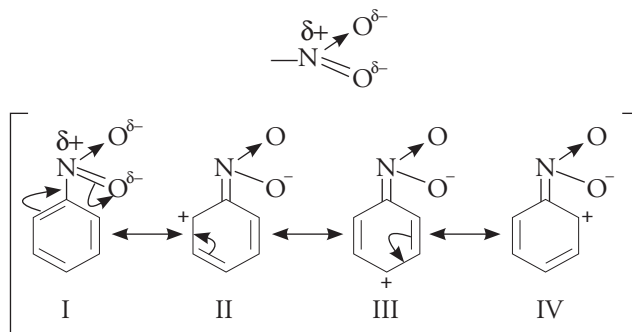
Resonance effect in chlorobenzene



($-I$ effect in chlorobenzene)

Deactivating groups: meta directors

The nitro group is a powerful electron withdrawing group. It withdraws electrons by both inductive effect ($-I$ effect) and resonance effect. Let us consider the resonating structures of nitrobenzene.



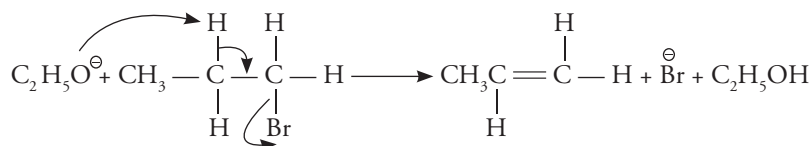
From the structures II, III and IV, it is clear that the electron density at *m* position is greater than at *o*- and *p*-position, hence the incoming groups attack the *m*- position. Owing to the $-I$ effect of $-\text{NO}_2$ group, it exerts deactivating influence.

19.9 Mechanism of Elimination Reactions

β -elimination reactions may proceed either by bimolecular (E2) or by unimolecular (E1) mechanism.

- (a) **Bimolecular Mechanism (E2)** This is a one-step process which involves the attack of a nucleophilic base on the β carbon atom followed by the simultaneous loss of halide ion from α -carbon atom.

Consider the example of the action sodium ethoxide on 1-bromopropane when propene is formed.



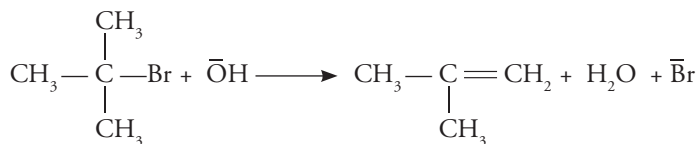
The rate of the reaction depends on the concentration of both the substrate and the base. The rate of reaction for the above reaction is

$$\text{Rate} = k [\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}] [\text{C}_2\text{H}_5\text{O}^\ominus]$$

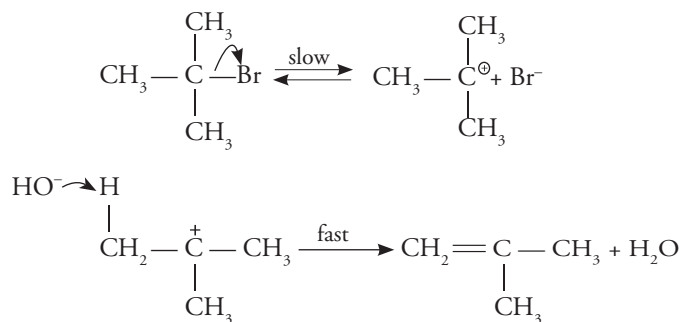
or for a general elimination reaction

$$\text{Rate} = k [\text{Substrate}] [\text{Base}]$$

- (b) **Unimolecular Mechanism (E1)** These elimination reactions occur in two steps. The first step which is the rate-determining step involves the formation of carbocation (analogous to $\text{S}_\text{N}1$ mechanism). The attack of base occurs in the second step. Let us consider the example of the action of strong solution of alcoholic alkali on 2-bromo-2-methylpropane (t-butylbromide).



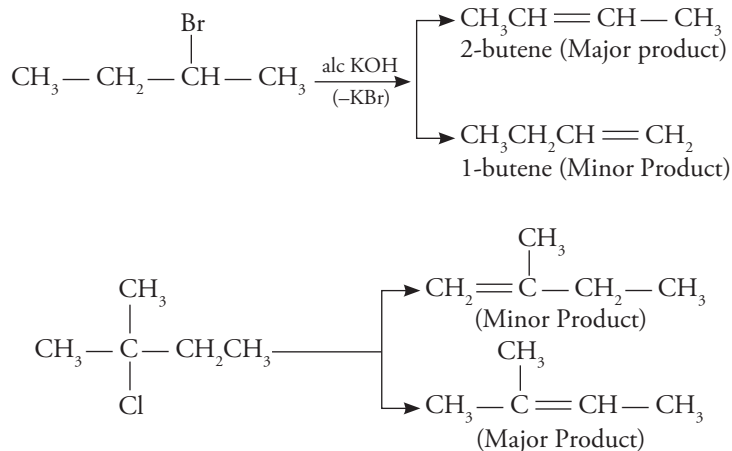
Mechanism



$$\text{Rate of reaction} = k [(\text{CH}_3)_3\text{C Br}]$$

Hence the reaction follows first order kinetics. The first step involves ionisation of the substrate forming carbocation. In the second step, the carbocation thus formed loses a β -proton with the help of the base forming the final elimination product.

Saytzeff Rule This rule states that during the elimination reaction that alkene is formed preferably which has greater number alkyl groups attached to the double bond.

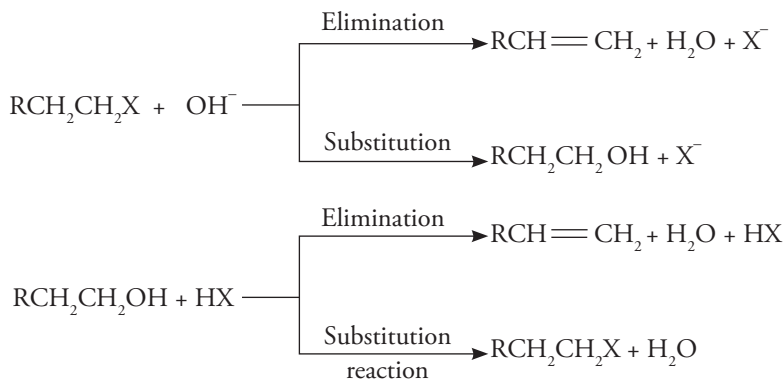


The preferential formation of more substituted alkenes in the above reactions can be correlated to the relative stabilities of various alkenes. The greater stability of more substituted alkenes can be explained on the basis of hyperconjugation.



Elimination versus Substitution

As discussed earlier both E1 and S_N1 reactions proceed with the formation of intermediate carbocation and both require a base or nucleophile. Hence, elimination reactions can be accompanied by substitution reactions or it can be better said that the two compete with each other or occur simultaneously, for example



The factors favouring elimination or substitution reactions are given below

- (i) **Basic strength of reagent** A base is an electron pair donor or a proton abstractor. Therefore stronger bases favour elimination reactions (removal of proton) whereas weaker bases will merely substitute the group and hence favour substitution reaction. The decreasing basic strength of some bases is

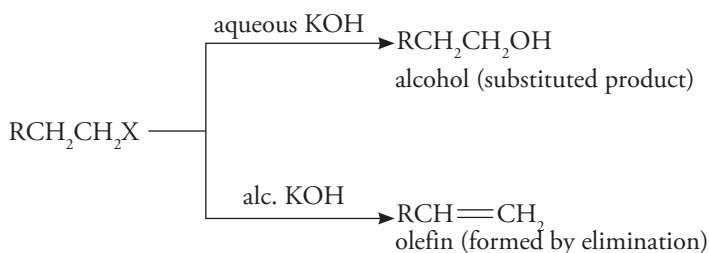


- (ii) **Ionising power of the solvent**

More ionising solvents favour substitution reactions and less ionising solvents favour elimination reactions. The ionising power of some solvents is



This has been proved by the fact that alkyl halides undergo substitution reactions in the presence aqueous KOH solution and elimination reaction in the presence of alcoholic KOH solution.



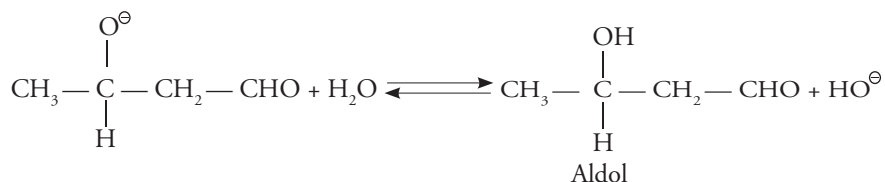
- (iii) **Concentration of the reagent** Higher concentration of base favours elimination reactions.
 (iv) **Effect of temperature** Elimination reactions are favoured by high temperatures.

Practice problems

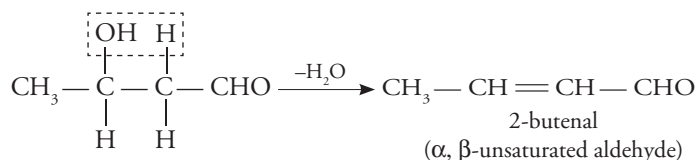
Give reasons why

- Propene reacts with HBr to give isopropyl bromide and not n-propyl bromide.
- C_6H_6 although highly unsaturated, undergoes substitution reactions.
- Carbonyl compounds are reactive towards nucleophilic reagents, but alkenes are not reactive towards such reagents.
- Alkyl chloride reacts with aqueous KOH to form alcohols, whereas in the presence of alcoholic KOH alkenes are formed as major products.
 (Hint: aqueous KOH gives OH^- ions which act as nucleophile whereas alc KOH gives ethoxide ion $\text{C}_2\text{H}_5\text{O}^-$ which are more basic than OH^- ions and brings about elimination.)
- Haloalkanes are more reactive than haloarenes.

(iii) The anion so formed accepts hydrogen from the solvent molecule to form the product.

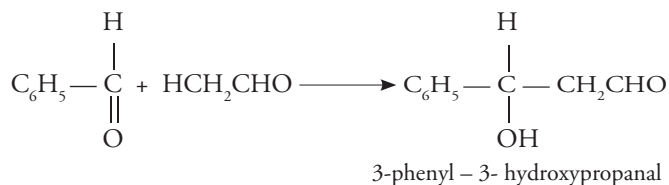
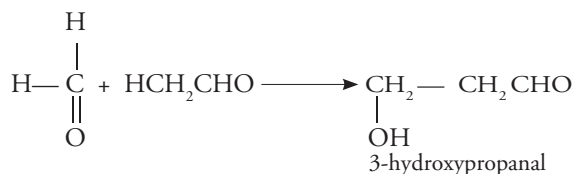


In the presence of dilute acids and bases the aldol may eliminate a water molecule to form α, β -unsaturated aldehyde.



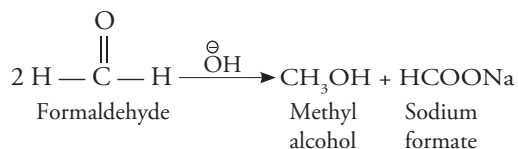
Crossed aldol condensation

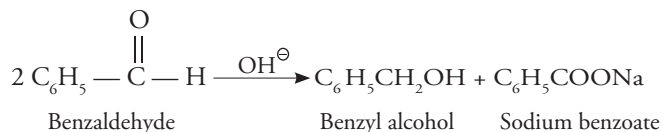
Crossed aldol condensation occurs between two different carbonyl groups. Different products can be formed. If both the aldehydes contain α -H atom, a mixture of four products is formed. These reactions are of little synthetic value. However, if one of the carbonyls does not possess α -hydrogen atom, then aldol condensation yields useful products.



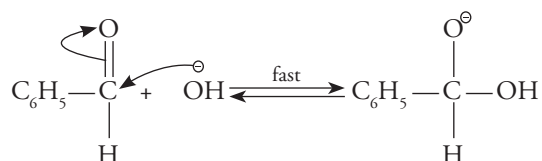
Cannizaro's Reaction

Aldehydes without α -H atoms, when treated with concentrated alkali undergo self oxidation and reduction to yield an alcohol and a salt of carboxylic acid. One molecule of an aldehyde is reduced to an alcohol at the cost of other, which is oxidised to a carboxylic acid.

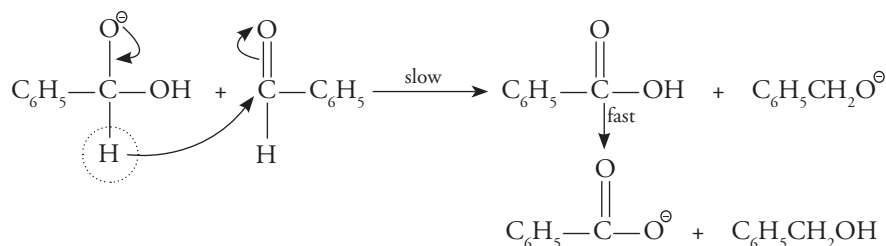


**Mechanism**

- (i) The aldehyde molecule reacts with the nucleophile (OH^\ominus).



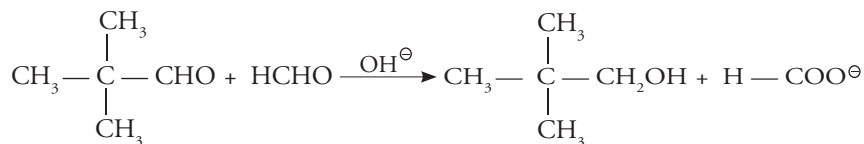
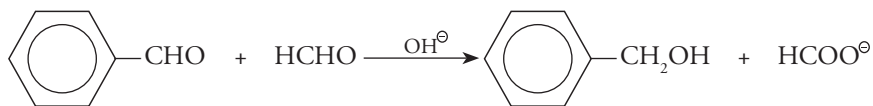
- (ii) This intermediate donates hydride ion to the carbonyl carbon of the second aldehyde molecule in the rate determining step.



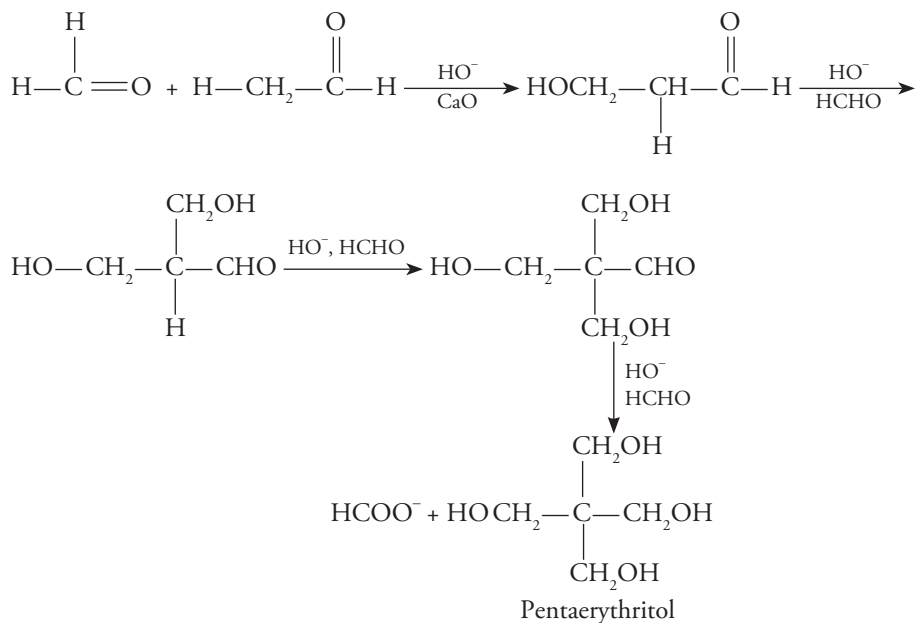
The final products are benzoate ion and benzyl alcohol.

Crossed Cannizaro's Reaction

Crossed Cannizaro's reaction takes place between two dissimilar aldehyde molecules forming a mixture of several products.

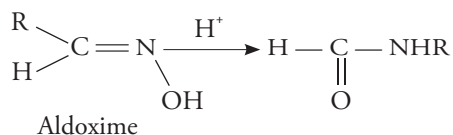
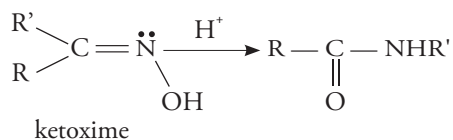


Industrial application of crossed cannizaros reaction coupled with aldol condensation is in the synthesis of pentaerythritol from formaldehyde and acetaldehyde.



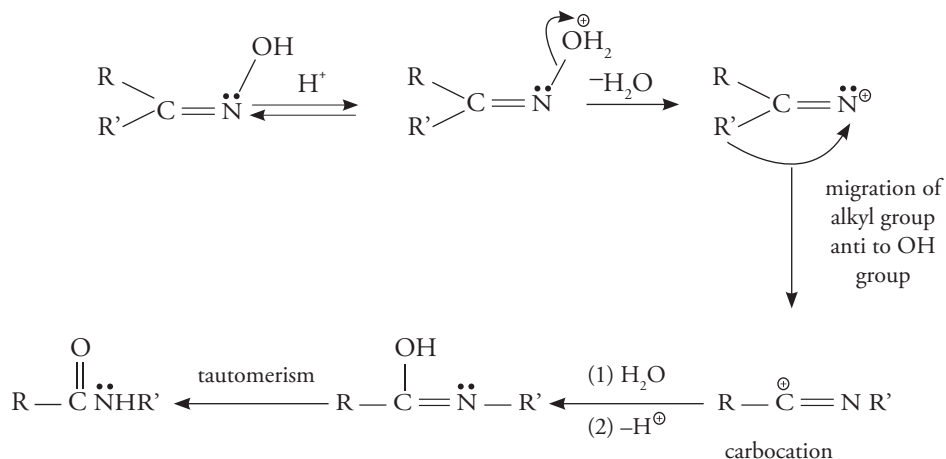
Beckmann Rearrangement

It involves the acid catalysed rearrangement of a ketoxime to N-substituted amide.

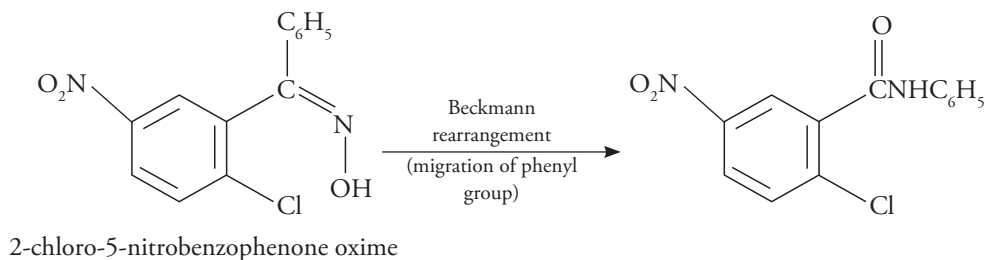


Mechanism

Acidic reagents like H_2PO_2 , H_2SO_4 , P_2O_5 , SOCl_2 , PCl_5 , etc. catalyse this rearrangement reaction. The mechanism is as follows.



The rearrangement is highly stereospecific in which the group anti to OH migrates. Migration of anti groups is proved further by the conversion of 2-chloro-5-nitrobenzophenone oxime to a chloronitrobenzanilide. It is found that the phenyl group, rather than the nitrated benzene ring, migrates to the nitrogen.

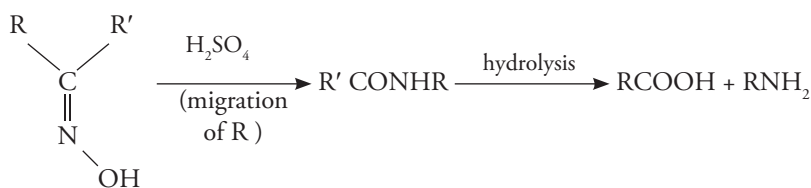


Applications

1. Determination of the configuration of ketoximes

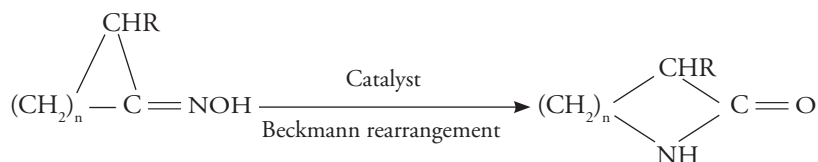
The *syn* and *anti* ketoximes yield different products. Hence the end products help in predicting the configuration of the ketoxime.

For example

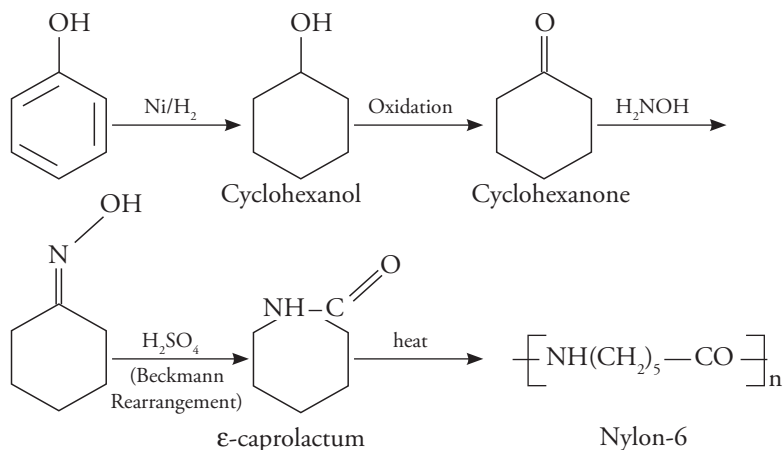




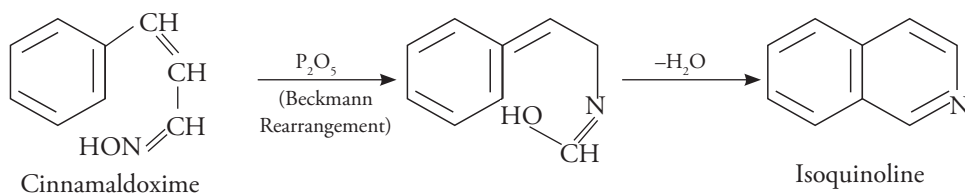
2. **Ring enlargement in cyclic ketoximes** Cyclic ketoximes undergo ring enlargement in the presence of a suitable catalyst.



This finds application in the synthesis of caprolactum by the Beckmann rearrangement of cyclohexanone oxime in the presence of concentrated sulphuric acid. ϵ -caprolactum on heating polymerises to give nylon-6



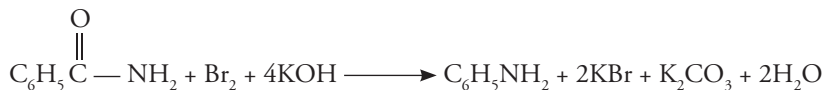
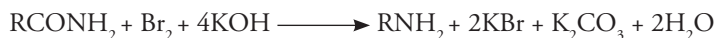
3. **Synthesis of Isoquinoline** Cinnamaldehyde oxime on Beckmanns rearrangement with acid yields isoquinoline.



Hoffmann Rearrangement or Hoffmann Degradation

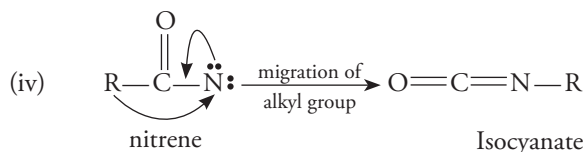
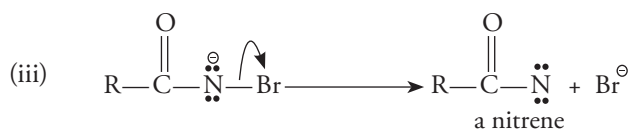
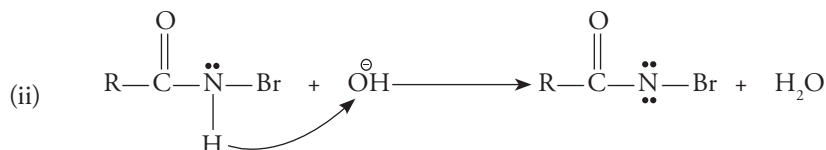
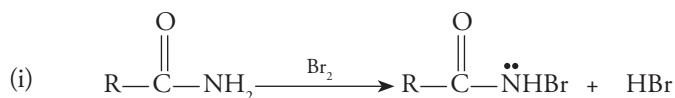
It is also known as Hofmann bromamide reaction. It involves the reaction of a primary amide with bromine in the presence of an alkali to yield primary amine with one carbon atom less than the parent amide.

This reaction is used for the preparation of primary amines.

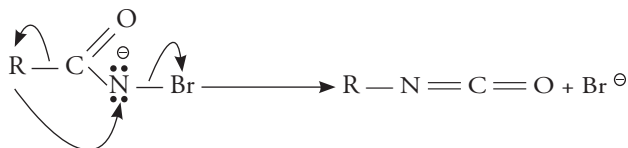


Mechanism

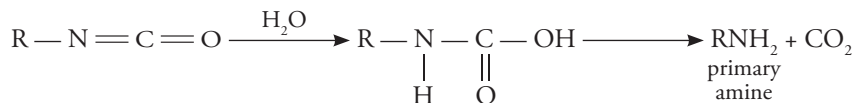
The reaction proceeds by the formation of intermediate nitrene followed by the migration alkyl group. Following steps are observed.



Steps (iii) and (iv) occur simultaneously, so that there occurs the loss of bromide ion and migration of alkyl group in the same step.

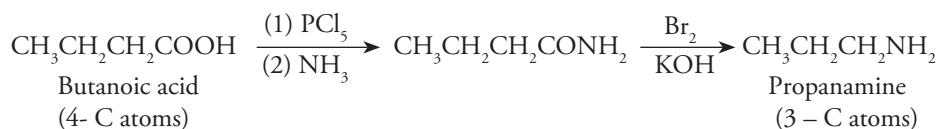


- (v) Hydrolysis of isocyanate takes place forming the primary amine.

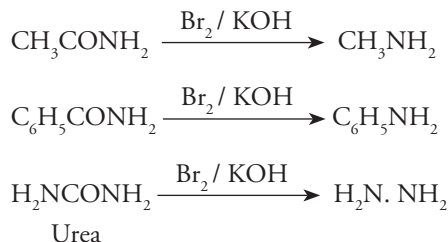


Applications

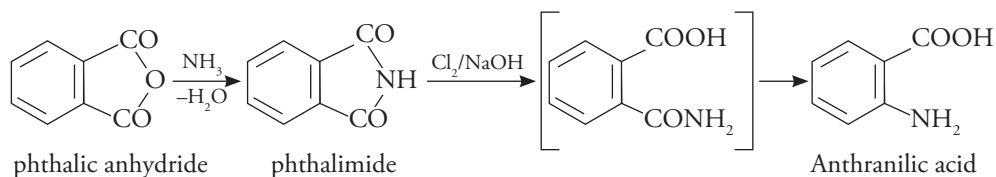
- (i) Hofmann reactions are used to step down the homologous series, that is, decrease the length of the carbon chain by one carbon atom.



- (ii) It is an important method for the preparation of primary amines.

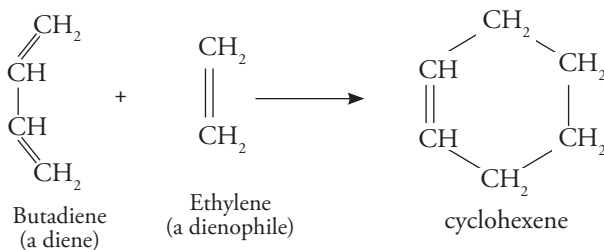


- (iii) **Preparation of aminoacids**

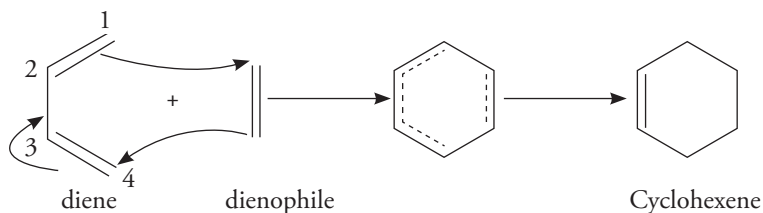


Diels–Alder Reaction

Diels–Alder reaction consists in addition of a conjugated diene to an unsaturated molecule called a dienophile, resulting in the formation of a six membered ring. The example is the reaction between butadiene and ethylene.



Diels–Alder reaction belongs to special class of reactions called pericyclic reactions, which are characterised by the making and breaking of two or more bonds in a single concerted step through cyclic transition states.

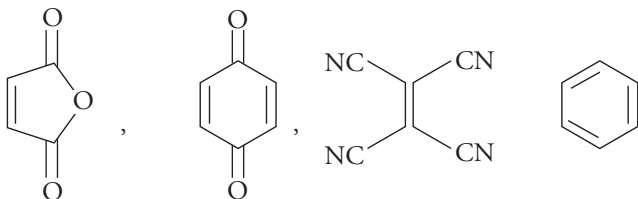


Since a cyclic product is formed via a cyclic transition state, these reactions are known as **cycloaddition reactions**. The above example involves addition between a 4π electron system (diene) and 2π electron system (dienophile), it is known as $[4 + 2]$ cycloaddition.

The rate of the above reaction is promoted by the presence of:

- (i) Electron-donating groups in the diene (like $-\text{CH}_3$ groups).
- (ii) Electron-withdrawing groups on the dienophile or the alkene (like $-\text{CHO}$, $-\text{COOR}$, $-\text{NO}_2$, $-\text{CN}$, etc.)

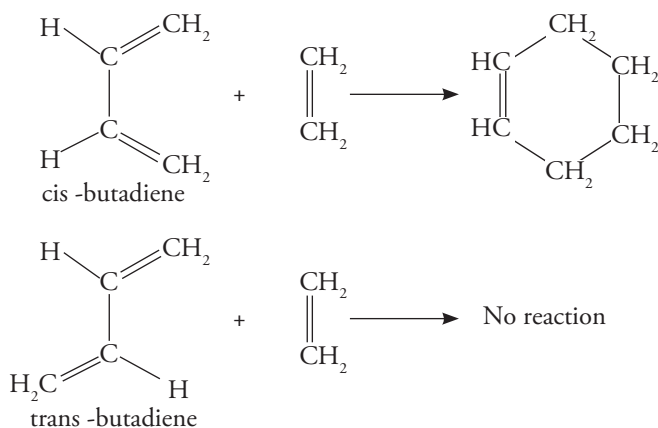
Reactive dienophiles are



Stereochemistry

The Diels–Alder reaction is stereospecific.

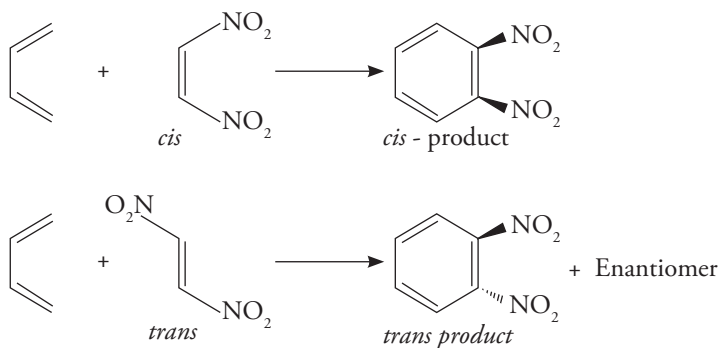
- (i) The *cis* form of diene takes part in the reaction to form the adduct. The *trans* form cannot form the adduct.



Trans dienes where transformation to *cis* form is not possible do not undergo the reaction.



- (ii) The Diels Alder reaction is also *cis* with respect to the dienophile, that is, groups lying *cis* to each other in the dienophile also lie *cis* to each other in the adduct. If they are *trans* on the dienophile, they form the *trans* product.



19.11 Stereochemistry

Stereochemistry is defined as the part of chemistry which deals with the study of three dimensional arrangement of atoms in space. It also studies the influence of this arrangement on the physical and chemical properties of these compounds.

Compounds having similar structure and connectivity but differing in their three dimensional arrangement in space are called stereoisomers and the phenomenon is called stereoisomerism. There are three types of stereoisomerism.

- (i) Optical isomerism
- (ii) Geometrical isomerism
- (iii) Conformational isomerism

Optical Isomerism

It is a kind of stereoisomerism in which the isomers differ in the spatial arrangement of atoms or groups of atoms. Optical isomers have same physical properties but differ in their behaviour towards plane polarised light. Let us see what is plane polarised light?

Plane polarised light

A beam of ordinary light has waves vibrating in all planes at right angles to the line of propagation. When this light is passed through a nicol prism (a special type of prism made of crystalline calcium carbonate), the vibrations in all but one plane are cut off (Fig. 19.7). Hence, the nicol prism converts an ordinary light into a plane polarised light.

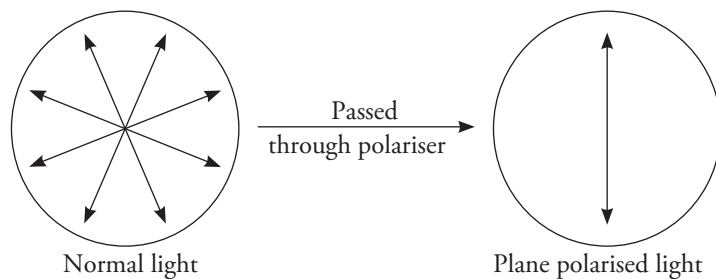


Figure 19.7 Normal and plane polarised light

When the solutions of certain organic compounds are placed in the path of plane polarised light they rotate the plane polarised light either to the left or to the right. Such substances which rotate the plane of polarised light either to the left or to the right are called optically active substances. Common examples of such substances are lactic acid, tartartic acid, glucose, fructose, etc.

This property of a substance by virtue of which it rotates the plane of polarised light is called optical activity.

All optically active substances do not rotate the plane of polarised light in the same direction. Some rotate the plane polarised light to the right (clockwise) while some compounds rotate the plane polarised light to the left (anticlockwise)

A substance which rotates the plane polarised light to the right is called dextro-rotatory. Such compounds are designated as *d* or by the sign(+) (latin dexter = right). Those compounds which rotate the plane of polarised light to the left are called laevo-rotatory (latin laevous-left). They are designated as *l* or by the sign(−). The angle through which the plane polarised light is rotated is called the angle of rotation. It is expressed as α (alpha).

The direction and magnitude of the rotation of plane polarised light by a substance is measured with the help of an instrument called polarimeter. It consists of a light source, two nicol prisms and a sample tube to hold the substance. The sample tube is placed between these two prisms as shown in Figure 19.8. The prism placed near the source of light is called polariser while the other placed near the eye is called the **analyser**. The aqueous solution is placed in a sample tube between the polariser and analyser and the rotation of the plane polarised light is observed.

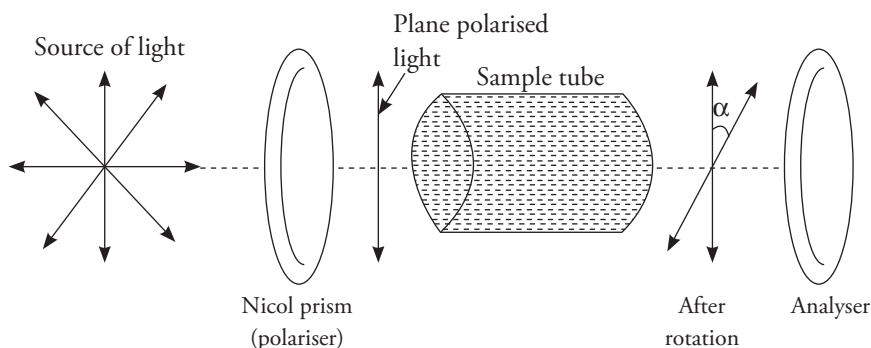


Figure 19.8 Rotation of path of plane polarised light

Optical Activity and Chirality

Let us now see what are the conditions that lead to optical activity. A study of the structure of optically active compounds reveals that all of them have non-superimposable mirror images. The molecules which are not superimposable on their mirror images are called **chiral** or **dissymmetric** molecules. The property of non-superimposability of a structure on its mirror image is called **chirality** or **dissymmetry**. The word chiral comes from Cheiros-Greek-hand. If we hold our right hand in front of a mirror the image looks like left hand. If we try to superimpose left and right hands (both palms down), we observe that the hands cannot be superimposed (Fig. 19.9). Therefore, hands are chiral. Other examples of chiral objects are gloves, shoes, etc. On the other hand, cup, fork, spoon and socks are identical with their mirror images. Such compounds or molecules which are superimposable on their mirror image are called achiral molecules.

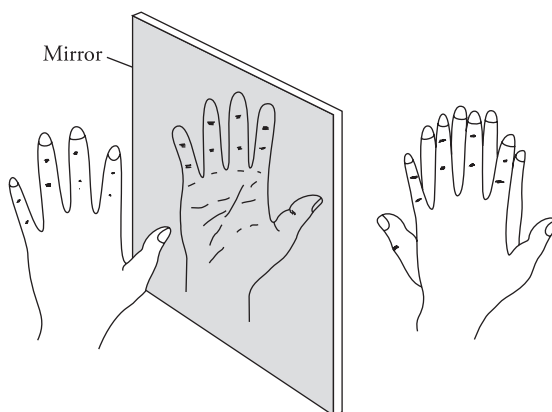
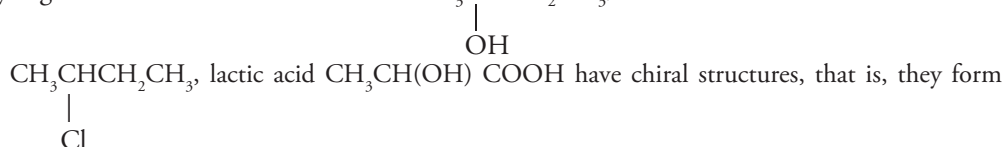


Figure 19.9 Non superimposable mirror image of a hand

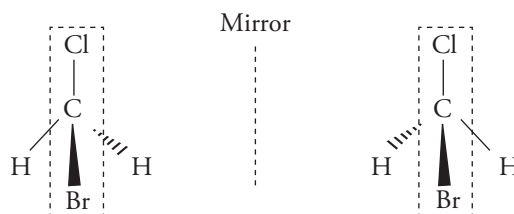
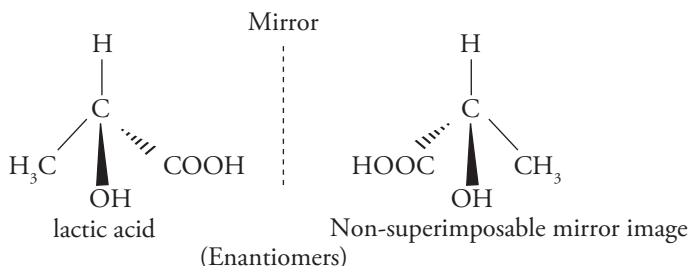
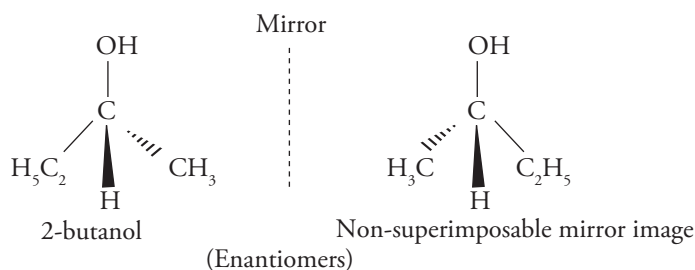
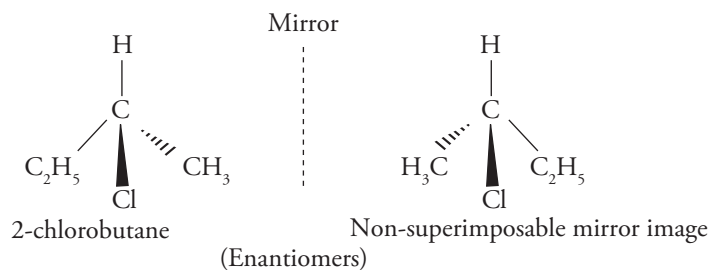
Many organic molecules such as 2-butanol $\text{CH}_3\text{CHCH}_2\text{CH}_3$, 2-chlorobutane



non-superimposable mirror images.

Dissymmetry and Plane of Symmetry

A plane of symmetry is an imaginary plane which bisects the molecule in such a way that the two halves are mirror images of each other. The plane may pass through atoms or between them. Chiral molecules do not have plane of symmetry and therefore they are called dissymmetric. On the other hand, achiral molecules have a plane of symmetry and are called symmetric.

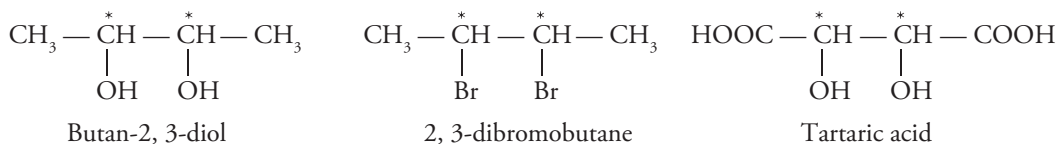


Mirror images: Superimposable

(Not enantiomers) The molecule possess plane of symmetry passing through Cl, C and Br.

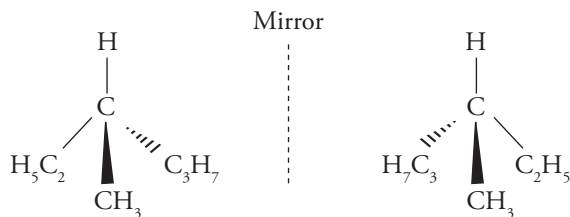
Thus dissymmetry is an essential condition for optical activity. A carbon atom bonded to four different atoms or groups of atoms is called a chiral carbon atom or asymmetric carbon atom. It is generally indicated as C*.

Some other molecules having asymmetric carbon atom are



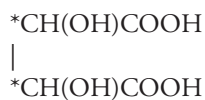
Enantiomers and their characteristics

Enantiomers or enantiomorphs are non-superimposable mirror images of each other. They have identical physical properties like melting points, boiling points, density, solubility, etc. Their chemical properties are also similar. They rotate the plane polarised light to exactly the same extent but in opposite directions. In other words they have the same specific rotation but of opposite sign. Enantiomers may be dextrorotatory (denoted by *d* or +) or laevorotatory (denoted by *l* or –) depending upon whether they rotate the plane polarised light to the right or to the left. For example, 3-methylhexane has asymmetric carbon atom and forms non-superimposable mirror images.

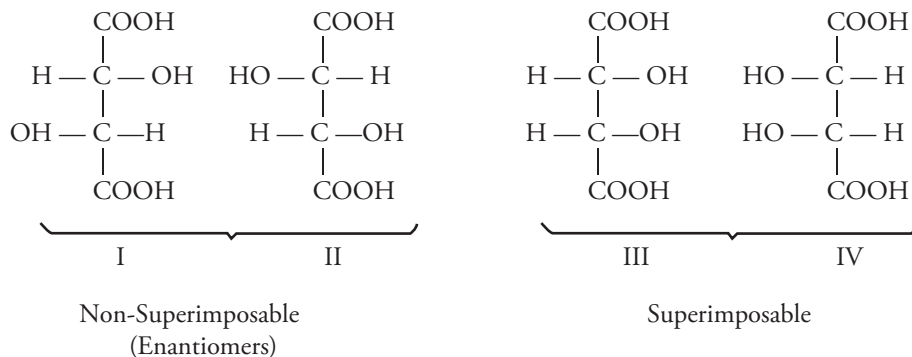


Enantiomers of 3 - methylhexane

Consider the example of tartaric acid having two asymmetric carbon atoms.



Since there are two asymmetric carbon atoms, four stereoisomers are possible (number stereoisomers = 2^n where n is the number asymmetric carbon atoms. Where *meso* compounds exist, the number of stereoisomers will be lesser than this maximum (discussed later). The stereoisomers of tartaric acid are

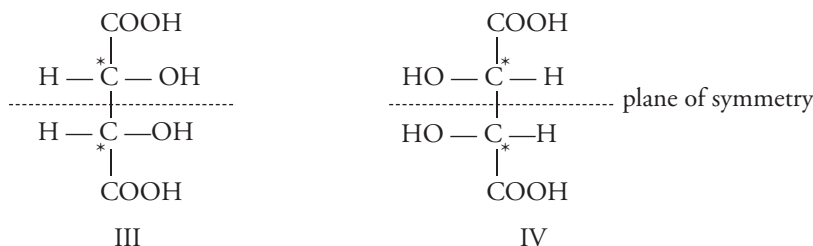


Structures I and II are enantiomers as they are non-superimposable mirror images. Similarly structures III and IV are also enantiomers. But how do structures I and II relate to structures III and IV? Structures I and II are stereoisomers of III and IV, but stereoisomer I is not the mirror image of either III or IV and so it is not an enantiomer of either one. A pair of stereoisomers that are not mirror images of each other are called diastereomers. Hence, the structures I and II are diastereomers of III and IV.

Diastereomers have different physical and chemical properties. Their physical properties like boiling points, solubilities, densities, refractive index, etc differ from each other. Their specific rotations are also different. They may have same or opposite signs of rotations or may be optically inactive also.

Meso compounds

Consider the following structures of tartaric acid.



Structures III and IV of tartaric acid are mirror images but they are not dissymmetric because the molecule has a plane of symmetry; one half of the molecule is mirror image of the other half. Hence in spite of having two chiral centres (denoted by *) the molecule is not chiral. It cannot exist in two enantiomeric forms and is optically inactive. It is called a meso compound.

A meso compound is one where molecules are superimposable on their mirror image even though they have chiral centres. The optical inactivity of a meso compound is due to **internal compensation**. One half of the molecule rotates the plane polarised light in one direction and the other half rotates it in the other direction. As a result the molecule is optically inactive.

Racemic Mixture

Racemic mixture is an equimolar mixture of the laevo and dextro rotatory enantiomers. It is represented as *dl* or \pm and will be optically inactive. The process of obtaining an optically inactive mixture from optically active *d* or *l* form is called racemisation. Racemic mixture is optically inactive due to **external compensation**. The (+) rotation caused by one enantiomer is cancelled by the rotation due to other enantiomer in the opposite direction (−).

Total number of Optical Isomers

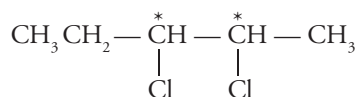
The number of optical isomers for a compound containing more than one asymmetrical carbon atoms can be calculated by the formulae given below

- (i) **Unsymmetrical molecules** $\text{C}_{ab}d \cdot \text{C}_{ab}e$

Number of *d* and *l* optical isomers = 2^n

(where *n* is the number of chiral carbon atoms)

Number of meso isomers = zero

Example - 2, 3 dichloropentane

$$n = 2 \quad \text{Hence total of optical isomers} = 2^n = 4$$

(ii) **Symmetric molecules** Cabc • Cabc $n = \text{even} (2, 4, 6, 8)$

$$d + l \text{ forms} = 2^{(n-1)}$$

$$\text{meso} = 2^{n/2-1}$$

$$\text{Total} = 2^{(n-1)} + 2^{(n/2-1)}$$

Example Tartaric acid $\text{CH}(\text{OH})\text{COOH} \bullet \text{CH}(\text{OH})\text{COOH}$

$$n = 2$$

$$d + l = 2^{(2-1)} = 2^1 = 2$$

$$\text{meso} = 2^{2/2-1} = 2^0 = 1$$

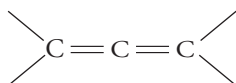
$$\text{Total} = 2 + 1 = 3 \text{ optical isomers (2 enantiomers + 1 meso compound)}$$

Optical isomerism in compounds containing no asymmetric carbon atom

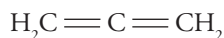
As studied earlier the primary requirement for a compound to be optically active is its non-superimposable mirror image. Most of the compounds are optically active due to the presence of an asymmetric or chiral carbon atom. However, there are some compounds which do not have a chiral carbon atom but the molecule as a whole is asymmetric (such molecules are better called dissymmetric) and hence optically active. Some compounds belonging to this category are

(i) **Allenes**

Allenes are compounds having the general formula

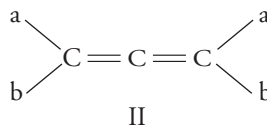
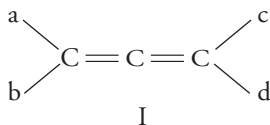


Allenes exhibit optical isomerism when the two groups attached to each terminal carbon atom are different.



Optically inactive

(groups on terminal carbon atom are the same)



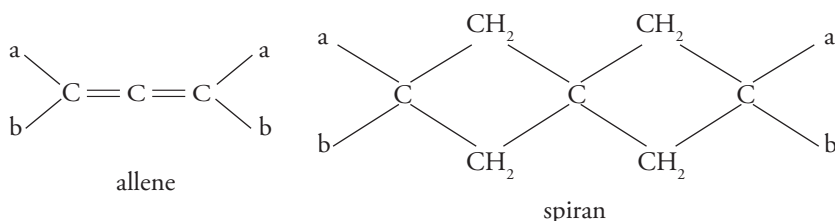
Optically active

(groups attached to terminal carbon atom are different)

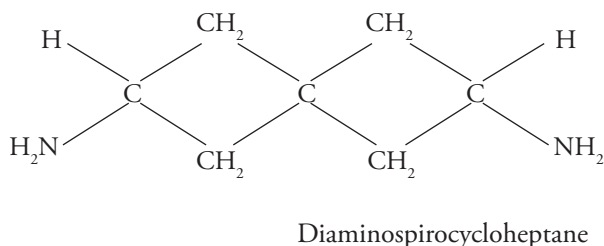
The above molecules I and II possess neither plane nor centre of symmetry and form non superimposable mirror image; hence, the allene molecule on the whole is asymmetric and optically active.

(ii) Spiro Compounds (Spirans)

A spiro compound (spiran) is formed by the replacement of both the bonds of allenes by rings.



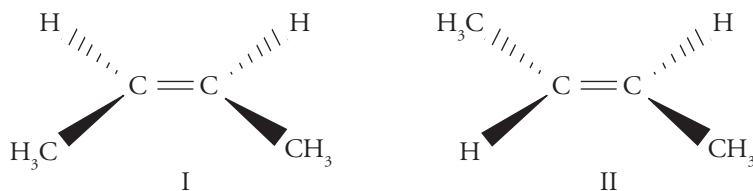
The two rings of spirans are perpendicular to each other and the molecule is dissymmetric, that is, it forms a non-superimposable mirror image and hence exhibits optical activity.



Geometrical Isomerism

The compounds that have the same structural formula but differ in the spatial arrangement of atom or group of atoms about the double bond are called geometrical isomers and the phenomenon is called geometrical isomerism.

Consider the example of 2-butene. We find that the atoms can be arranged in two different ways around the double bond.



The connectivity of atoms in the two isomers is the same and they differ only in the way the atoms are oriented in space. In structure I, both the methyl groups lie on the same side, whereas they lie on opposite sides in structure II. These structures cannot be converted into one another by simple bond rotation. They can be converted only by breaking the π bond, which requires extra energy of about 70 kcal/mol. This energy is not available at room temperature. Because of this energy barrier

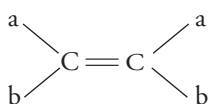
there is hindered rotation around the carbon carbon double bond. As a result of this hindered rotation, the structures I and II exist separately and have been isolated.

Structures I and II are stereoisomers, but as the two are not mirror images, they are called diastereomers.

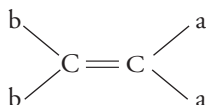
Structure I in which both the methyl groups lie on the same side is called *cis* (latin: on this side) and structure II in which both the methyl groups are on opposite sides is called *trans* (latin: across). Geometrical isomers differ in their physical properties. *Cis* isomers where bulky groups are on the same side are less stable than *trans* isomers where the groups are well separated.

The essential condition for geometrical isomerism is that

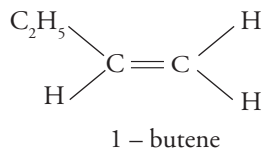
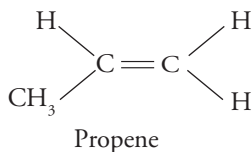
- The molecule must have a double bond
- Different atoms or groups must be attached to the same carbon atom.



Different groups attached to
same carbon atom
(shows geometrical isomerism)

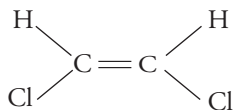


Similar groups attached to same
carbon atom
(Does not show geometrical isomerism)

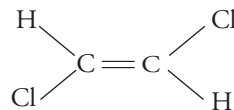


No geometrical isomerism

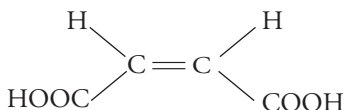
Other examples of geometrical isomerism are



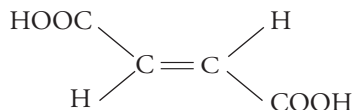
cis –1, 2 dichloroethene



trans –1, 2 dichloroethene

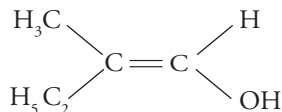
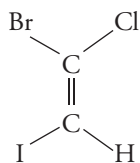


Maleic acid



Fumaric acid

This system using *cis* and *trans* prefixes works well for disubstituted alkenes, but what if all the groups are different?



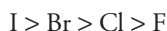
The *cis*, *trans* system cannot be applied to the above compounds. Such compounds are specified using the E – Z system.

E – Z nomenclature

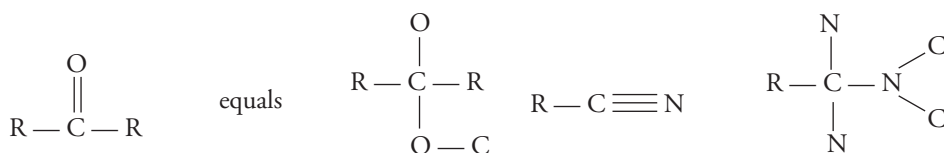
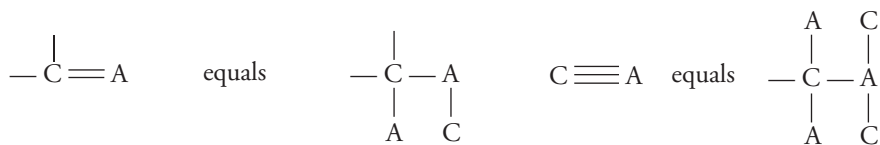
When three or four different groups are attached to the carbon atom of a double bond, then the E–Z system is used. Z means on the same side (German: Zusammen together) and E means on opposite side (German: entgegen-opposite).

The E–Z system is based on the assignment of priorities to the atoms or groups attached to each carbon atom of the double bond. The priority is assigned according to Cahn–Ingold–Prelog (CIP) sequence rules which are discussed below.

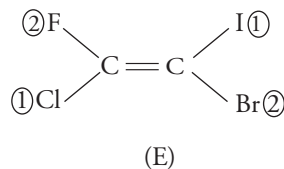
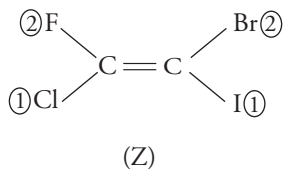
1. The atom with higher atomic number gets the highest priority. For example, if the four atoms attached are F, Cl, Br and I, then the priority becomes



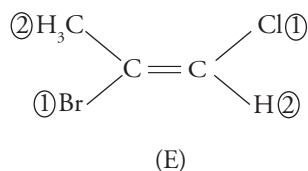
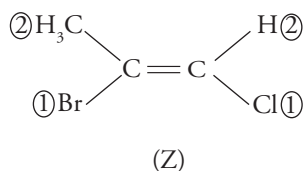
2. If two isotopes of the same element are present, the isotope of higher mass gets the higher priority. For example, deuterium (D) gets priority over hydrogen (H).
3. If the first atom of the two substituents is identical, then the next atom is considered for priority assignment. For example, ethyl group gets priority over methyl group. Similarly, –COOH gets priority over –CHO.
4. If double, or triple-bonded groups are present as substituents, both atoms are considered to be duplicated or triplicated. For example



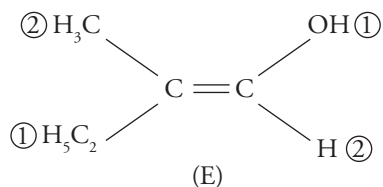
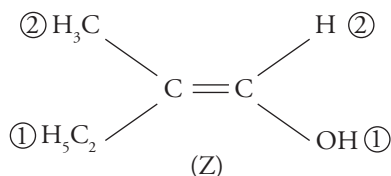
According to E–Z system, priorities are assigned to the groups attached to the double bonds. If the two groups of higher priority are on the same side of the double bond, the isomer is a Z isomer and if the two higher priority groups are on the opposite sides of the double bond, the isomer is called E isomer.

For example

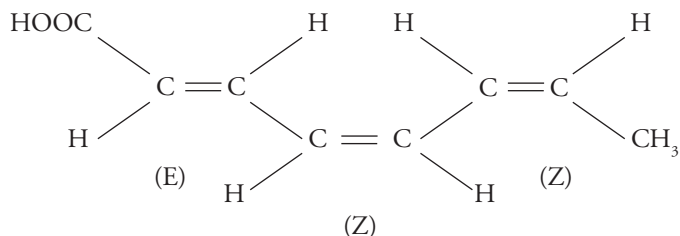
Priority $\text{Cl} > \text{F} : \text{I} > \text{Br}$



Priority $\text{Br} > \text{CH}_3 : \text{Cl} > \text{H}$

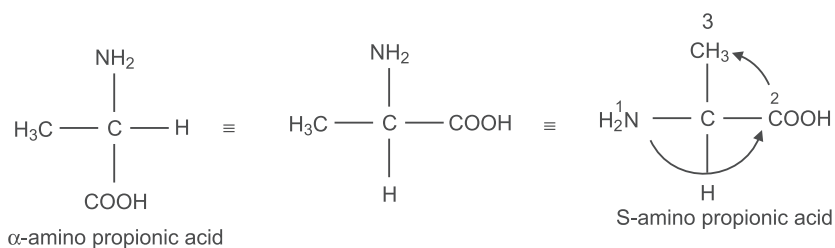
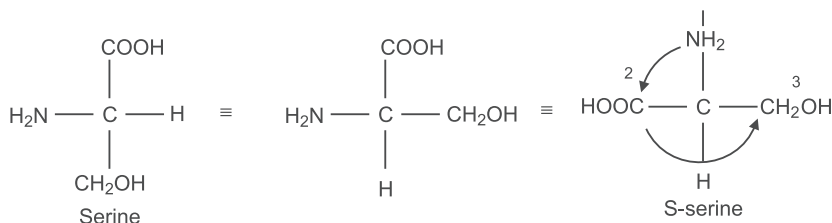
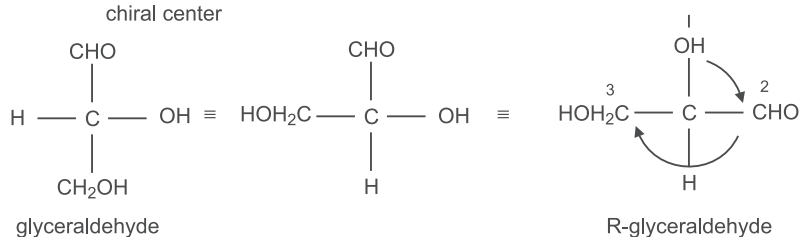
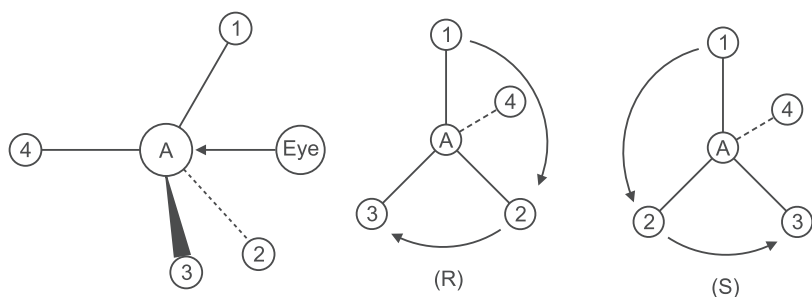


Priority $\text{C}_2\text{H}_5 > \text{CH}_3 : \text{OH} > \text{H}$

**Absolute configuration**

Absolute configuration defines the arrangement of atoms around the chiral centre. It makes use of the sequence rules given by Cahn–Ingold–Prelog. To decide the configuration of the molecule the ligands are sequenced according to the rules mentioned above. They are arranged in the order of decreasing precedence, that is, $1 > 2 > 3 > 4$.

- The molecule is viewed from the side farthest away from the ligand of lowest priority (i.e., ligand 4) and the directions of decreasing precedence of ligands 1, 2 and 3 are determined.
- If the order of precedence $1 \rightarrow 2 \rightarrow 3$ is clockwise then the molecule is assigned the configuration R (from the latin word *rectus* = right) and if it is anticlockwise then the configuration assigned to the molecule is S (*sinister* = left).
- If the molecule is represented by the Fischer projection formula then the group of least priority should be written at the bottom of the projection formula but it may not always be the case. In case the group of least priority is not at the bottom, then it is brought at the bottom by two (or even) number of exchanges of groups around the asymmetric atom. If odd number of exchanges are made, then the enantiomer is formed.
- The above explanation are illustrated by the examples given below:

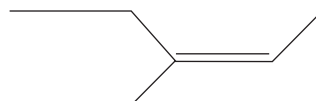
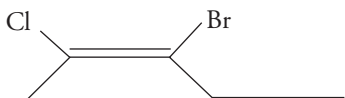
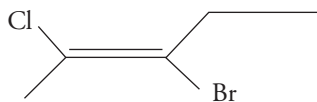
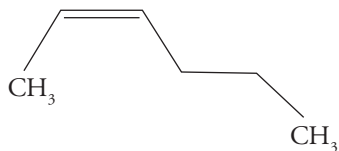
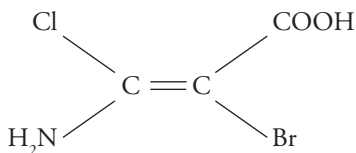
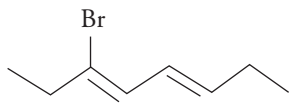
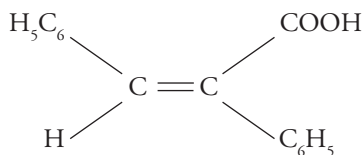
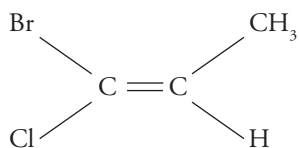




Practice Problems

Give reasons why

1. 2-butene exists in two isomeric forms, but not 1-butene.
2. Butan-2-ol is optically active, whereas butan-1-ol is optically inactive.
3. Assign E and Z to the following compounds



4. Which of the following compounds will show optical isomerism



Conformational Isomerism in Hydrocarbons

This type of isomerism arises due to rotation about carbon–carbon single bond. The carbon–carbon single bond in alkanes is a sigma bond and has cylindrical symmetry. As a result, the rotation about the carbon–carbon single bond is quite free. Therefore, a large number of spatial arrangements of the atoms or groups of atoms attached to the carbon atoms are possible. These different spatial arrangements are called conformations. Thus, the different arrangement of atoms in a molecule which can be obtained due to rotation about carbon–carbon single bond are called conformations.

Conformations of ethane

In the ethane molecule ($\text{CH}_3\text{--CH}_3$), the two carbon atoms are bonded by single covalent bond. If one of the methyl groups is kept fixed and the other is rotated about the C–C bond an infinite number of arrangements of the hydrogen atoms attached to one carbon with respect to the other carbon atom are possible. These infinite number of different arrangements are called conformations. However, two conformations are important. These are

(i) Staggered conformation

(ii) Eclipsed conformation

(i) **Staggered conformation** In this type of arrangement, the hydrogens on the two carbon atoms are staggered with respect to each other. They are at maximum distance from each other and the repulsion between them is minimum. Hence the stability is maximum.

(ii) **Eclipsed conformation** In this type of conformation the hydrogen of the second carbon atom are right behind the hydrogen atoms of the first carbon atom. Consequently the repulsion between them is maximum. The conformations can be represented by two kinds of formulae.

Saw horse projections

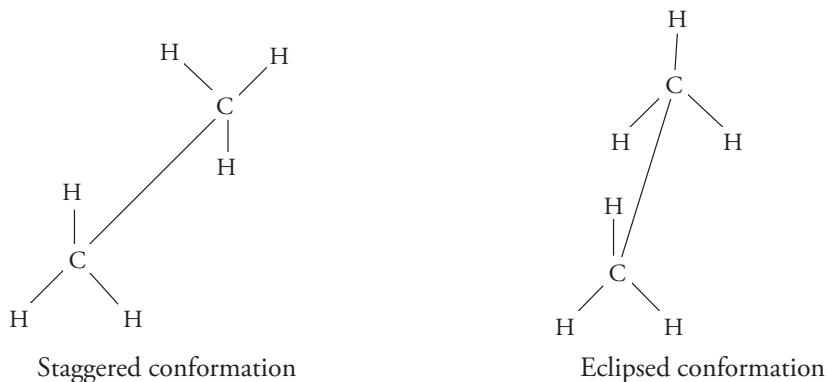


Figure 19.10 Saw horse projection formulae of ethane

Newman projections

In these projections, the two carbon atoms forming the σ bond are represented by two circles, one behind the other so that only the front carbon is seen. The C–H bonds of the front carbon are depicted from the centre of the circle. The C–H bonds of the rear carbon atom are drawn from the circumference of the circle (Fig. 19.11).

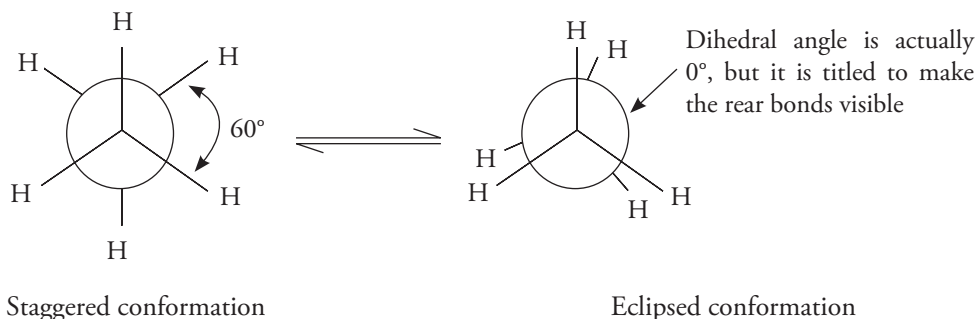


Figure 19.11 *Newman projection formulae of ethane*

When a staggered conformation is rotated through an angle of 60° it changes to eclipsed conformation and when the eclipsed conformation is rotated by 60° it again changes to staggered conformation.

Apart from staggered and eclipsed conformations infinite number of intermediate conformations are the possible. These conformations are called skew conformations.

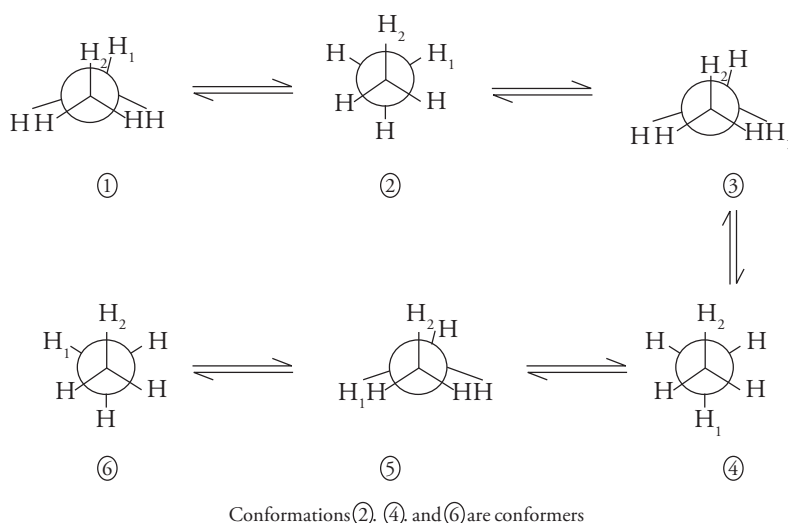


Figure 19.12(a) *Conformations of ethane*

Relative Stabilities of Conformations of Ethane

The different conformations of ethane differ in their relative stabilities. In staggered conformation the hydrogen atoms are at a maximum distance apart (dihedral angle is 60°) and hence the force of repulsion is minimum making it energetically stable. In eclipsed conformation there is maximum repulsion between the hydrogen atoms (dihedral angle 0°) and hence its energy is more and hence stability is less. The difference in energy contents of staggered and eclipsed conformation is 3 kcal mol^{-1} . However, this energy difference is not large enough to prevent rotation. Even at ordinary temperatures, the two forms keep converting into each other and it is not possible to isolate them.

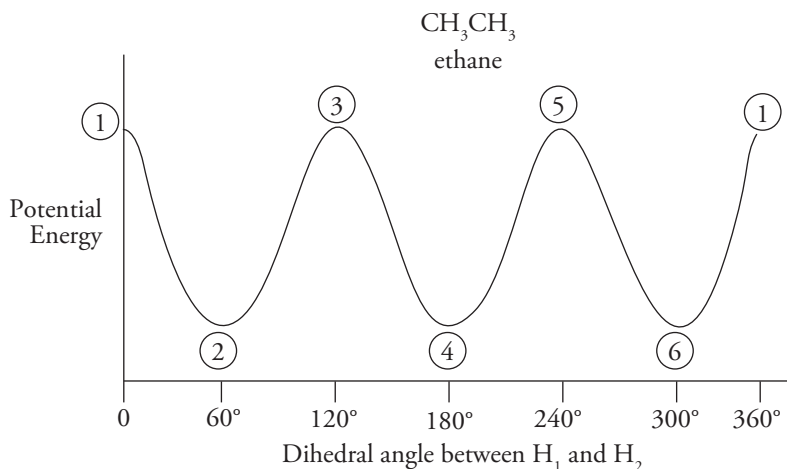


Figure 19.12(b) Potential energy of various conformers of ethane

Conformations for butane

In butane the rotation about C_2 and C_3 bond is of interest because of the relative positions of the two methyl groups. Focussing attention on C_2 and C_3 due to the presence of methyl groups the following positions are observed (Fig. 19.13 a).

Structure I which is a fully eclipsed conformation. All the methyl groups and hydrogen atoms are aligned completely. There is maximum steric or van der Waals repulsion between the groups and hence its potential is maximum and it is unstable. This is the **syn** conformation.

On rotating the front carbon atom by 60° we get another conformation in which the two methyl groups are separated by 60° . The dihedral angle between the two methyl groups is 60° . It is a staggered conformation called **gauche** conformation and the potential energy is lesser than the **syn** conformation (conformations II and VI are gauche conformation).

On further rotating the front carbon atom by 60° , as eclipsed conformation (III) is obtained in which the CH_3 group is aligned with H atom.

A further rotation of 60° gives the most stable conformation called **anti** conformation (IV). It is a staggered conformation in which the dihedral angle between the two methyl groups is 180° . The steric repulsion is minimum and hence the stability is maximum. The anti-conformation is more stable than gauche conformation by 0.8 kcal/mol .

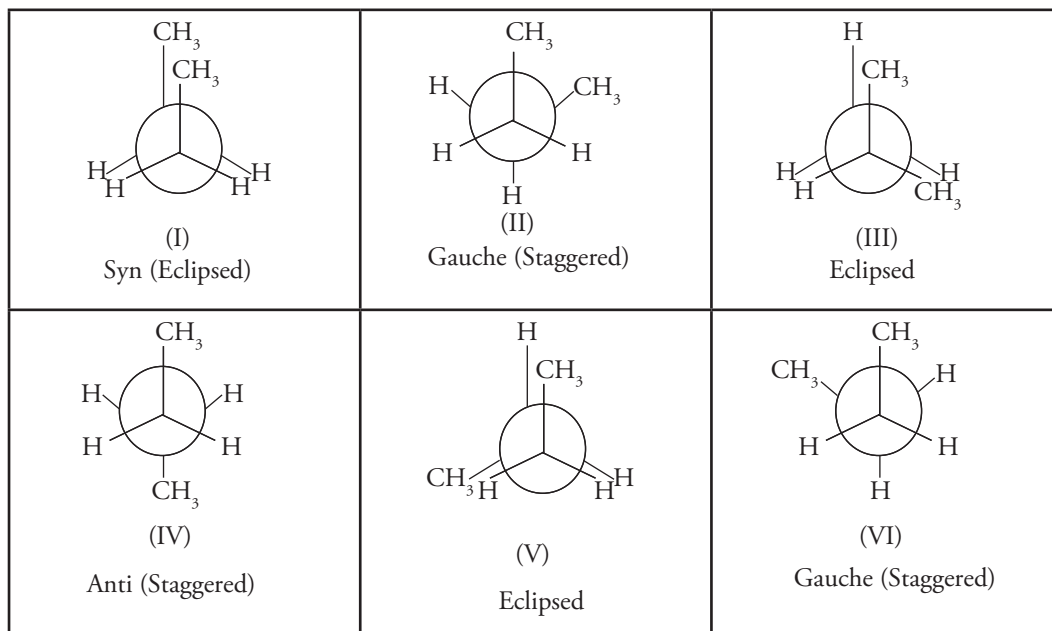


Figure 19.13(a) Conformations of butane

The potential energy curve for the various conformations of butane is given below.

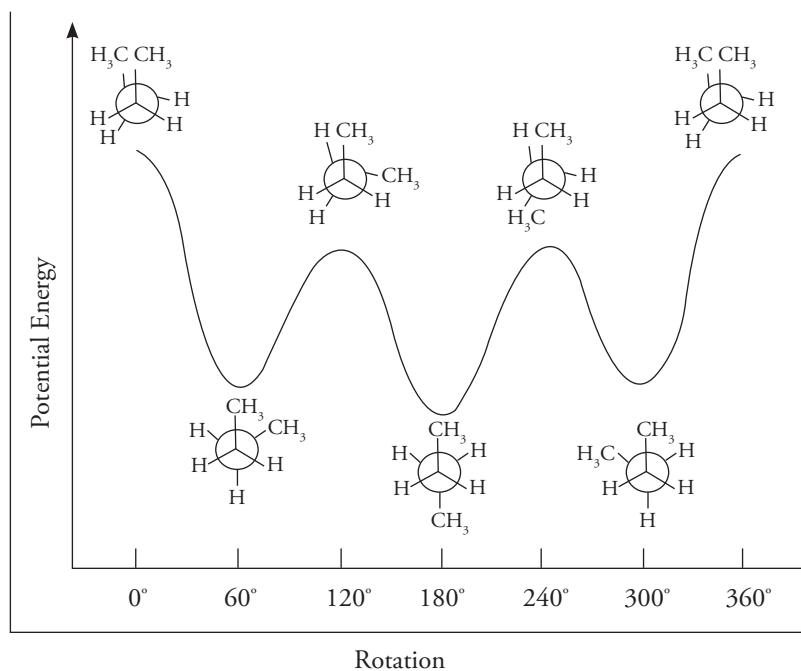


Figure 19.13(b) Potential energy of various conformers of butane

Conformations of cyclohexane

The cyclohexane molecule is quite stable. It avoids strain by assuming a conformation in which all the bond angles between carbon atoms are close to the tetrahedral angle of $109^\circ 28'$. Therefore it adopts a non-planar structure. Moher in 1918 postulated the **puckered ring conformations** for cyclohexane having all the angles as tetrahedral. These two puckered conformations are **chair conformation** or **Z form** and **boat conformation of C form**.

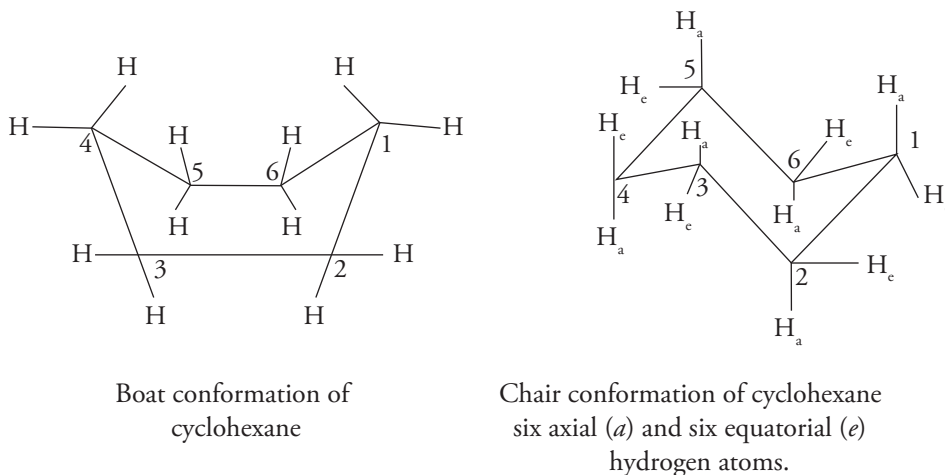


Figure 19.14 Boat and chair conformations of cyclohexane

Stabilities of conformations of cyclohexane

The chair **conformation** of cyclohexane is more stable than the boat conformation due to the following reasons.

- (i) In chair conformation the adjacent hydrogen atoms on all the neighbouring carbon atoms are quite staggered and the force of repulsion between them is minimum. However, in boat conformation, the adjacent hydrogen atoms on C_2-C_3 and C_5-C_6 atoms are eclipsed.
- (ii) The two hydrogen atoms marked as H_f bonded to the C_1 and C_4 atoms in boat conformation are quite close and they repel each other.

Therefore the energy of boat conformation is more than that of chair conformation.

Therefore, cyclohexane exists mainly in the chair form.

19.12 Drugs

Drugs are chemicals that interact with the macromolecular targets to produce a biological response. When the biological response is therapeutic assisting in the diagnosis, treatment or prevention of a disease it is termed as a medicine. However, some drugs are also used as a stimulant arising a state of euphoria and can be habit forming leading to addiction.

Drugs are classified into different categories depending on certain criteria like their chemical structure, physical and psychological effects. Drugs affect the nervous system of individuals and create varied responses. Brief classification of drugs based on their physical and psychological effects is given below:

Analgesics like aspirin reduce pain.

Anti-inflammatory drugs reduce inflammation in the body.

Antipyretics reduce body temperature.

Depressants are drugs that suppress the activity of brain and nerves. These drugs are administered to relieve anxiety and promote sleep.

Stimulants increase the activity of the brain and nervous system making an individual more energetic and ecstatic. They can also make an individual paranoid and induce anger.

Hallucinogens are drugs that act on the central nervous system. They alter the perception of space, time and reality and the individual may start imagining things and situations that are not real.

Opioids are used to treat pain and cough.

Inhalants exist in vapour state at room temperature and are consumed by inhaling

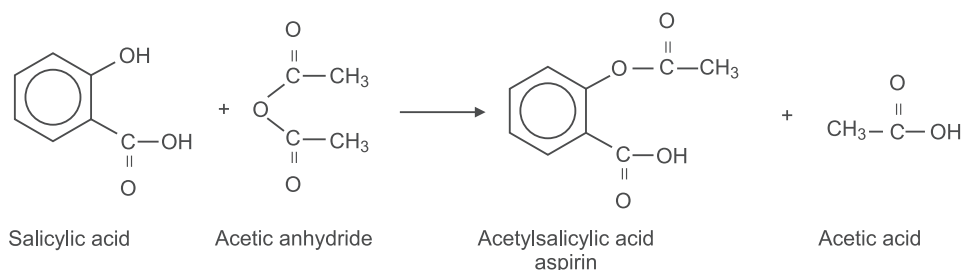
Antibiotics were earlier defined as chemicals produced from microorganisms used to kill or inhibit the growth of other microorganisms. Now since they can be artificially synthesised hence now they are defined as molecules that either kill or inhibit the growth of microorganisms.

Psychoactive drugs affect the functioning of the central nervous system and alter mood, perception and consciousness

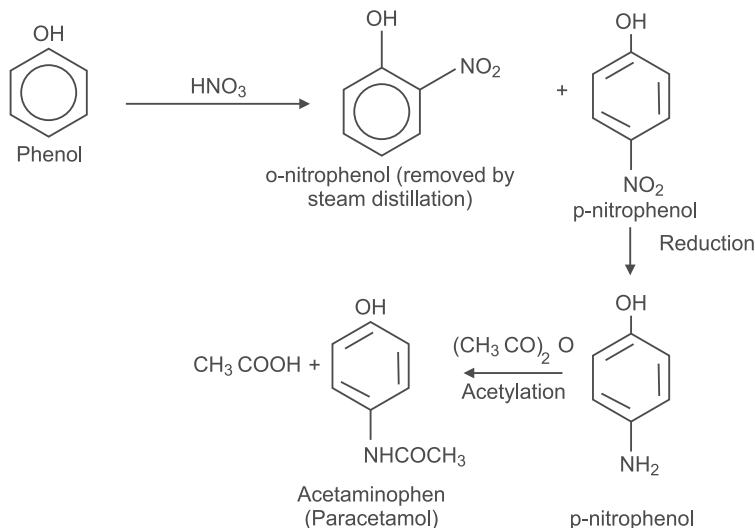
Cannabis is an illicit drug used worldwide as charas, bhang and ganja.

There are several other ways of classifying drugs. It should be remembered that most of the drugs serve medicinal purpose only in small quantity and have side effects if consumed in larger quantities. Here we shall discuss two commonly used drugs aspirin and paracetamol

Aspirin: It is a common drug used to reduce fever (antipyretic) and as an analgesic to relieve pain. Chemically it is acetyl salicylic acid prepared by the reaction of salicylic acid with acetic anhydride.



Paracetamol: It is one of the most common drug used to reduce fever and in the treatment of mild pain like headache, pain in joints, muscles and body pain. It is prepared by the nitration of phenol which gives both ortho and para-nitro phenol. The ortho isomer is removed by steam distillation and the para isomer is reduced to give p-aminophenol which on acetylation gives acetaminophen widely known as paracetamol. Although it causes lesser gastrointestinal side effects as compared to aspirin but overdose of paracetamol causes damage to liver.



Summary

- Organic chemistry is the study of the compounds of carbon.
- Organic compounds are made up of covalent bonds. During chemical reactions these bonds undergo two types of cleavage:

Homolytic cleavage The bond breaks symmetrically and both the atoms retain one electron of the electron pair. It results in the formation of free radicals.

Heterolytic cleavage When the electronegativities of the two atoms is different unsymmetrical bond cleavage occurs and the bond pair is retained by the more electronegative atom.

- The organic compound which undergoes reaction (termed as substrate) is attacked by another reagent (termed as attacking reagent). Attacking reagents are of two types-

Electrophiles or electrophilic reagents They are electron loving species. They are themselves electron-deficient and can be positively charged (e.g., H^+ , H_3O^+ , NO_2^+ , etc.) or electrically neutral species (e.g., BF_3 , AlCl_3 , carbenes, etc.) having an incomplete octet.

Nucleophiles or nucleophilic reagents They are nucleus loving species. They are electron-rich and can be negatively charged (e.g., Cl^- , Br^- , OH^- , NH_2^- , etc) or neutral species with lone pair of electrons (e.g., $\text{H}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{O}}-\text{H}$, $\text{R}-\ddot{\text{S}}-\text{H}$, etc.).

- The electrons of the covalent bonds in organic molecules undergo displacement either under the influence of the substituents (inductive and resonance effect) or under the influence of the attacking reagents (electromeric effect and inductomeric effect).
- Inductive effect and mesomeric or resonance effects are permanent effects while electromeric and inductomeric effects are temporary effects.

- Inductive effects and inductomeric effects are transmitted along the sigma bonds of the carbon chain whereas mesomeric and electromeric effects operate through the π electron system.
- Inductive effect is of two types

Negative inductive effect (–I effect) Substituent which pulls the electron pair towards itself is said to exert –I effect (e.g., NO_2 , CN , halogens, OH , OCH_3 , C_6H_5 , etc.).

Positive inductive effect (+ I effect) Electron releasing substituents are said to exert +I effect (e.g., R_3C , R_2CH , RCH_2 , CH_3 , etc.).
- Inductive effect decreases as length of carbon chain increases.
- In mesomeric effect the π electrons are transferred from a multiple bond to single bond, or to an atom or the lone pair of electrons are transferred to single bond.
- Resonance stabilises the structure. More the resonating structures more stable is the molecule. Energy of resonating structure is less than the energy of individual structures.
- Resonance effect can be electron releasing (+ M or + R) or electron withdrawing (–M or –R)
- Both resonance and inductive effect influence bond length, dipole moment, reactivity, strength of acids and bases, etc.
- Electromeric effect (represented by E), takes place under the influence of attacking reagent. It can be + E (electron transfer towards the attacking reagent) or –E (electron transfer away from the attacking reagent).
- Hyperconjugation (Baker Nathan affect) occurs in system having at least one α hydrogen attached to unsaturated carbon atom. The C–H bond of α carbon atoms release electron by a mechanism similar to electromeric effect. It is also called no bond resonance.
- Various reaction intermediates are

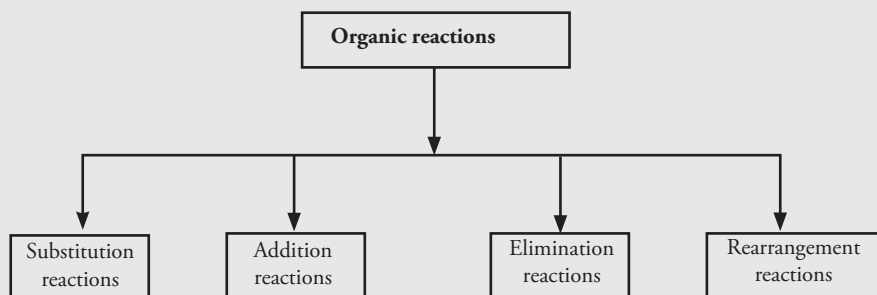
Free radicals Formed by homolytic cleavage, represented as C^\bullet , can be sp^2 hybridised or sp^3 hybridised.

Carbonium ions or carbocations Carbon atom bears positive charge with six electrons in its valence shell, represented as C^+ , it is sp^2 hybridised with planar geometry.

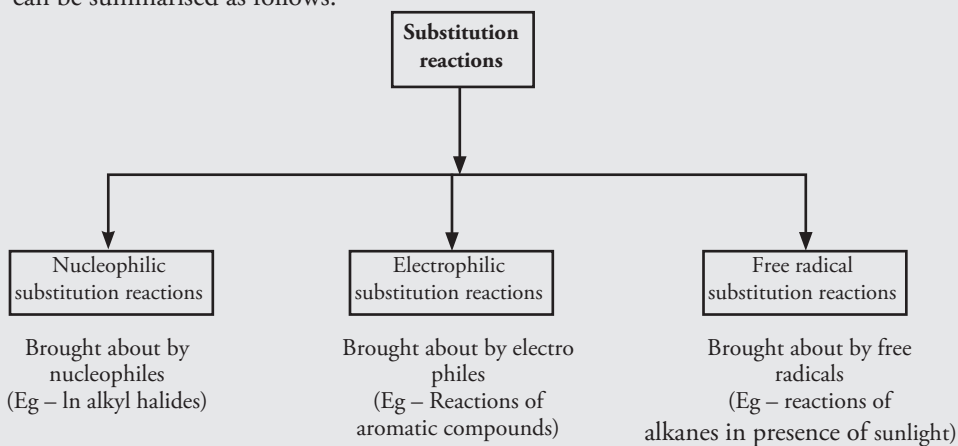
Carbanions Carbon atom is trivalent with two extra electrons which are not bonded, represented as C^- , sp^3 hybridised with pyramidal geometry.

Carbenes Short lived, neutral, divalent carbon with two unpaired electrons, represented as :CH_2 . It can exist in singlet and triplet states.

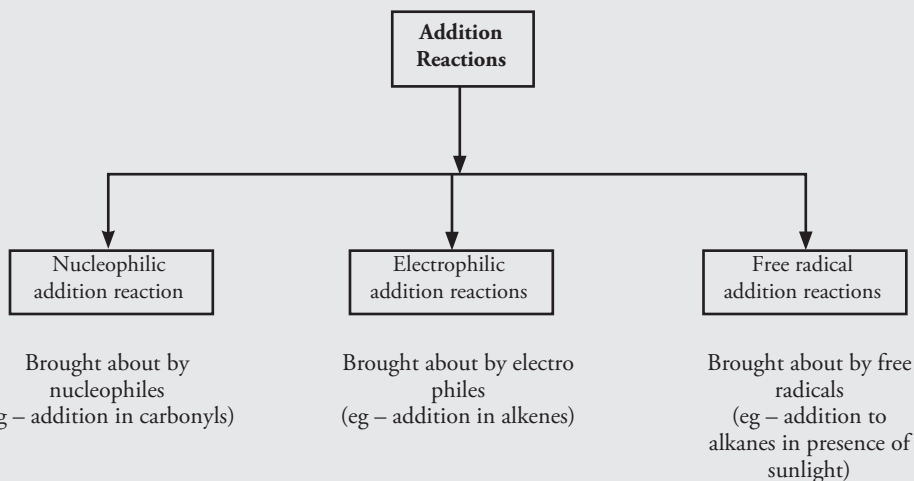
Nitrenes Nitrogen atom has one bond pair and two lone pairs. Represented as $\text{:}\ddot{\text{N}}\text{:}$. It can exist in singlet and triplet states.
- Types of Organic Reactions**
Organic reactions are of four types.



Substitution reaction When one atom of a molecule is replaced by the other. They can be summarised as follows.



- Nucleophilic substitution reactions can follow S_N1 or S_N2 mechanism. S_N1 mechanism proceeds in two steps by the formation of intermediate carbocation. S_N2 mechanism occurs in one step (bimolecular) by the rear attack of the nucleophile.
- **Addition reaction** Where attacking reagent adds on the substrate molecule.



- **Elimination reactions** Atoms or groups of atoms are removed from a molecule. When the removal occurs from adjacent carbon atoms it is called β elimination (leads to unsaturation), when it occurs from same carbon atom it is called α elimination (leads to the formation of carbenes).
 β elimination can be single step (E2 mechanism) or two step (E1 mechanism) process.
- **Rearrangement reactions** These reactions involve migration of an atom or group of atoms to another position.
- **Markownikoffs rule** It states that when addition occurs across an unsymmetrical alkene, the more electronegative part of attacking reagent goes to the carbon atom with lesser number of hydrogen atoms.
- **Saytzeff rule** It states that during elimination reactions that alkene is formed preferably which has greater number alkyl groups attached to the double bond.
- Stereochemistry deals with the three dimensional arrangement of atoms in space. Compounds having similar structure but different three dimensional arrangement in space are called stereoisomers.
- Stereoisomers which rotate the plane polarised light are said to be optically active.
- Optically active compounds should form non-superimposable mirror images. They have a chiral carbon atom and lack elements of symmetry like plane of symmetry and centre of symmetry.
- Enantiomers are non-superimposable mirror images of each other. They differ in their behaviour towards plane polarised light. If they rotate plane polarised light to right it is called dextrorotatory and if it rotates plane polarised to the left it is called laevorotatory.
- Diastereomers are a pair of stereoisomers that are not mirror images of each other.
- Meso compounds have plane of symmetry and are optically inactive inspite of having chiral centre or asymmetric carbon atom.
- Racemic mixture is formed by mixing equimolar amounts of dextro and laevorotatory enantiomers.
- Allenes and spirans are optically active inspite of not having a chiral carbon atom.
- Geometrical isomerism occurs in compounds having different arrangement of atoms around the double bond.
- Geometric isomers can be *cis* (when similar groups are on the same side of double bond) or *trans* (when similar groups are on opposite sides of the double bond.)
- The E – Z system of nomenclature is used to name those compounds in which all atoms around the double bond are different. The atoms or groups are assigned priority according to the sequence rules. If the atoms of higher priority are on the same side of the double bond then it is a Z isomer and if they are on opposite sides then it is an E isomer.
- Conformational isomerism arises due to rotation about the carbon–carbon single bond.

- Drugs are chemicals that interact with the macromolecular targets to produce a biological response. When the biological response is therapeutic assisting in the diagnosis, treatment or prevention of a disease it is termed as a medicine.
- Drugs are classified on the basis of their chemical structure, physical and psychological effects. The common categories are *analgesics* like aspirin reduce pain, *anti-inflammatory* (reduce inflammation), *antipyretics* (reduce body temperature), *depressants* (suppress the activity of brain and nerves), *stimulants* (increase the activity of the brain and nervous system), *hallucinogens* (act on the central nervous system and alter the perception of space, time and reality), *opioids* (used to treat pain and cough), *inhalants* (drugs that are consumed by inhaling), *antibiotics* (they kill or inhibit the growth of microorganisms), *psychoactive drugs* (affect central nervous system and alter mood, perception and consciousness), *cannabis* (an illicit drug used worldwide as charas, bhang, ganja).

Review Questions

1. Explain electrophilic and nucleophilic reagents with the help of suitable examples.
2. What is inductive effect? Explain the effect of inductive effect on the following:
 - (i) Bond length
 - (ii) Dipole moment
 - (iii) Reactivity of alkyl halides
 - (iv) Strength of carboxylic acids
 - (v) Basic nature of amines
3. Define resonance. What are the essential conditions for resonance?
4. With the help of suitable examples, explain the effect of resonance on the following:
 - (i) Bond length
 - (ii) Strengths of acids and bases
5. What is hyperconjugation? How does it influence the following:
 - (i) Bond length
 - (ii) Stability of alkenes
 - (iii) Directive influence of alkyl benzene
 - (iv) Stability of carbocation.
6. Distinguish between inductive and electromeric effects giving suitable examples.
7. What are free radicals. What are the various factors influencing the stability of free radicals.
8. How are carbocation formed? Explain the factors responsible for the stability of the carbocation.
9. Define a carbanion. How can it be generated? Discuss its structure and stability.

10. Write short notes on the following:
 - (i) Carbenes
 - (ii) Inductomeric effect
 - (iii) Electromeric effect
 - (iv) Nitrenes
 - (v) Free radicals
11. Explain the following:
 - (i) Addition reactions
 - (ii) Substitution reactions
 - (iii) Elimination reactions
 - (iv) Rearrangement reactions
12. Both alkenes and carbonyl compounds contain double bonds and undergo addition reactions. Explain the difference between the addition reactions of alkenes and carbonyls with the help of suitable examples.
13. Giving suitable example, explain the following:
 - (i) Markownikoffs rule
 - (ii) Anti Markownikoffs rule or peroxide effect
 - (iii) Satyzeff rule
14. What is S_N1 reaction? Explain why S_N1 mechanism leads to the formation of racemic mixture.
15. Write down the mechanism of S_N2 reactions and discuss the stereochemical aspect of the reaction.
16. Explain the factors affecting reactivity and mechanism of nucleophilic substitution reactions.
17. Compare and contrast S_N1 and S_N2 reactions.
18. Explain the mechanism of electrophilic substitution reactions taking the example of nitration of benzene.
19. Why are alkyl, OH, NH_2 groups *o* and *p* directing and activating? On the other hand, explain why halogens inspite of being *o*, *p* directing deactivate the benzene ring.
20. Explain why meta directing groups invariably deactivate the benzene ring.
21. Discuss in detail the mechanism of elimination reactions.
22. Elimination and substitution reactions compete with each other. Discuss.
23. Explain the mechanism of the following:
 - (i) Aldol condensation
 - (ii) Cannizaros reaction
 - (iii) Beckmann rearrangement
 - (iv) Hofmann rearrangement or Hofmann degradation
 - (v) Diels–Alder reaction
24. Explain the following:
 - (i) Optical isomerism
 - (ii) Dissymmetry and Plane of symmetry
 - (iii) Enantiomers
 - (iv) Diastereomers
 - (v) Meso compounds
 - (vi) Racemic mixture

25. Optical activity is generally shown by compounds having a chiral centre. However some compounds do not have a chiral centre but are still optically active. Explain with suitable examples.
26. What is geometrical isomerism? What are the essential conditions for a compound to show geometrical isomerism?
27. Explain the E – Z system of nomenclature. In what way it is better than the cis-trans nomenclature?
28. What is conformational isomerism? Draw the potential energy diagram for the various conformations of n-butane.
29. Explain the sequence rules for deciding the priority of a side group.
30. Draw the Newmann projections of all the conformations of butane. Explain their relative stability with the help of the potential energy diagram.
31. What are enantiomers and diastereomers? Explain with the help of 2-bromo-3-chlorobutane.
32. What are drugs? Explain the different common categories of drugs. Also explain the preparation, properties and uses of paracetamol and aspirin.

Multiple Choice Questions

1. Which of the following species has a positively charged carbon atom
 - (a) Carbanion
 - (b) Carbocation
 - (c) Carbene
 - (d) Free radical
2. The least stable carbocation is
 - (a) Tertiary alkyl
 - (b) Secondary alkyl
 - (c) Primary alkyl
 - (d) Methyl
3. Which of the following species has a trigonal planar shape
 - (a) CH_3^+
 - (b) CH_3^-
 - (c) BF_4^-
 - (d) SiH_4
4. Which of the following is not a nucleophile
 - (a) OH^-
 - (b) HSO_3^-
 - (c) BF_3
 - (d) NH_3
5. Which of the following species shows sp^2 hybridisation
 - (a) NH_3
 - (b) CH_3^+
 - (c) PH_3
 - (d) SbH_3

6. Which of the following groups has highest inductive effect
 - (a) CH_3-
 - (b) CH_3CH_2-
 - (c) $(\text{CH}_3)_2\text{CH}-$
 - (d) $(\text{CH}_3)_3\text{C}-$
7. Shifting of electrons of a multiple bond under the influence of a reagent is called
 - (a) I effect
 - (b) M effect
 - (c) E effect
 - (d) T effect
8. Which among the following molecules can behave both as an electrophile and as a nucleophile
 - (a) CH_3Cl
 - (b) CH_3CN
 - (c) CH_3NH_2
 - (d) CH_3OH
9. Which of the following is the strongest acid
 - (a) CH_2FCOOH
 - (b) CH_2ClCOOH
 - (c) CH_2BrCOOH
 - (d) CH_2ICOOH
10. The basic character of amines is in the order
 - (a) $t > s > p$
 - (b) $p > s > t$
 - (c) $s > p > t$
 - (d) None
11. A permanent effect in which π electrons are transferred from a multiple bond to an atom or to a single covalent bond is
 - (a) Mesomeric effect
 - (b) Electromeric effect
 - (c) Hyperconjugation
 - (d) Inductive effect
12. The process of electron release due to the presence of the system $\text{H}-\text{C}-\text{C}=\text{C}$ is known as
 - (a) Tautomeric effect
 - (b) Hyperconjugation
 - (c) Mesomeric effect
 - (d) Electromeric effect
13. In the singlet and the triplet states of carbene, the unshared electrons are respectively
 - (a) Unpaired, unpaired
 - (b) Paired, unpaired
 - (c) Paired, paired
 - (d) Unpaired, paired
14. In $\text{S}_{\text{N}}2$ mechanism there is
 - (a) Partial racemization
 - (b) Complete racemization
 - (c) Complete inversion
 - (d) Partial inversion and mostly racemization
15. The reaction $\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Br}^-$, is an example of
 - (a) Nucleophilic substitution
 - (b) Electrophilic substitution
 - (c) Nucleophilic addition
 - (d) Electrophilic addition

16. Both alkyl halides and aromatic compounds undergo substitution reactions. The difference between the two is that alkyl halides undergo _____ substitutions, whereas aromatic compounds undergo _____ substitution reactions.

- (a) Electrophilic, electrophilic (b) Nucleophilic, electrophilic
(c) Electrophilic, nucleophilic (d) Nucleophilic, nucleophilic

17. Tick the wrong statement

- (a) Carbonyls undergo nucleophilic addition reactions whereas alkenes undergo electrophilic addition reactions.
(b) Addition of HBr on alkene in the presence of peroxides is an example of free radical addition reaction.
(c) α -elimination or 1,1 elimination leads to the formation of carbenes
(d) S_N1 substitution reaction occurs in single step and the product is formed with inverted configuration.

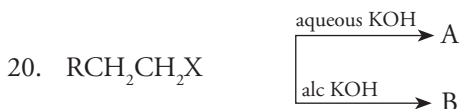
18. Match the following for electrophilic substitution reactions

- | | |
|-------------------------------|--|
| (i) Halogenation | (a) $\text{HNO}_3 + \text{H}_2\text{SO}_4$ |
| (ii) Nitration | (b) Concentrated sulphuric acid |
| (iii) Sulphonation | (c) Alkyl halides in presence of Lewis acids |
| (iv) Friedal craft alkylation | (d) Halogen in presence of FeCl_3 , ZnCl_2 |

- (a) (i) d (ii) a (iii) b (iv) c
(b) (i) a (ii) b (iii) c (iv) d
(c) (i) b (ii) d (iii) c (iv) a
(d) (i) d (ii) c (iii) a (iv) b

19. Which of the following groups is an ortho-para directing and a deactivating group

- (a) OH (b) Cl
(c) NH_2 (d) NO_2



A and B are, respectively

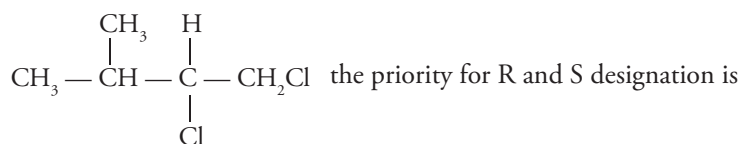
- (a) Alkene and alcohol (b) Alcohol and alkene
(c) Alcohol and alcohol (d) Alkene and alkene

21. Aldehydes without α -hydrogen atoms when treated with concentrated alkali undergo self oxidation and self reduction to yield an alcohol and a salt of carboxylic acid. The reaction is termed as
- (a) Aldol condensation (b) Friedel crafts reaction
(c) Cannizaros reaction (d) Beckmann rearrangement
22. Which of the following reaction proceeds via nitrene intermediate
- (a) Hofmann degradation or Hofmann rearrangement
(b) Beckmann rearrangement
(c) Aldol condensation
(d) Diels Alder reaction
23. Reactions that proceed via cyclic transition state are termed
- (a) Cycloaddition reactions (b) Elimination reactions
(c) Substitution reactions (d) Addition reactions
24. A compound whose atoms are superimposable on the mirror image even though they contain asymmetric carbon atoms is called
- (a) A meso compound (b) An erythro isomer
(c) A threo isomer (d) A racemic mixture
25. A molecule is divided into two halves which are mirror images of each other by
- (a) Centre of symmetry (b) A plane of symmetry
(c) An axis of symmetry (d) All the above
26. The R and S notation of compounds containing chiral carbon atom is determined by _____ priority system
- (a) Robinson–Ingold–Prelog (b) Cahn–Ingold–Prelog
(c) Cahn–Prelog–Langmuir (d) Prelog–Robinson–Cahn
27. The dihedral angle between the C–H (as viewed along the C–C bond axis) in a staggered conformation of ethane is
- (a) 60° (b) 120°
(c) 180° (d) 240°
28. The six conformers of butane are
- (a) Four staggered and two eclipsed (b) Two staggered and four eclipsed
(c) All six staggered (d) Three staggered and three eclipsed

29. Match the conformers against the dihedral angle

- | | |
|---------------------------------|---------------------------------|
| (i) 300° | (a) Gauche ethane and butane |
| (ii) 120° | (b) Gauche ethane |
| (iii) 360° | (c) Eclipsed ethane and butane |
| (iv) 60° | (d) Eclipsed ethane |
| (a) (i) c (ii) d (iii) b (iv) a | (b) (i) b (ii) c (iii) d (iv) a |
| (c) (i) a (ii) b (iii) c (iv) d | (d) (i) b (ii) a (iii) d (iv) c |

30. In 1, 2-dichloro-3-methyl butane



- | | |
|--|--|
| (a) $(\text{CH}_3)_2\text{CH} > \text{CH}_2\text{Cl} > \text{Cl} > \text{H}$ | (b) $\text{Cl} > \text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CH} > \text{H}$ |
| (c) $\text{Cl} > (\text{CH}_3)_2\text{CH} > \text{CH}_2\text{Cl} > \text{H}$ | (d) $\text{CH}_2\text{Cl} > \text{Cl} > (\text{CH}_3)_2\text{CH} > \text{H}$ |

Solution

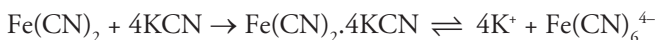
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|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (b) | 2 (d) | 3 (a) | 4 (c) | 5 (b) | 6 (d) | 7 (c) | 8 (b) |
| 9 (a) | 10 (c) | 11 (a) | 12 (b) | 13 (b) | 14 (c) | 15 (a) | 16 (b) |
| 17 (d) | 18 (a) | 19 (b) | 20 (b) | 21 (c) | 22 (a) | 23 (a) | 24 (a) |
| 25 (b) | 26 (b) | 27 (a) | 28 (d) | 29 (b) | 30 (b) | | |

Chapter 20

COORDINATION CHEMISTRY

20.1 Introduction

Coordination chemistry is the branch of chemistry that deals with the study of chemical, structural, magnetic and spectral properties of coordination compounds. Before having an insight into the properties of coordination compounds, it is essential to understand what are coordination compounds. Consider the example of potash alum $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. When this salt is dissolved in water, it dissociates into individual ions and the aqueous solution gives the test of all the constituent ions, that is, it gives the test of K^+ , Al^{3+} and SO_4^{2-} . Similarly aqueous solution of Mohr's salt $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ gives the test of Fe^{2+} , Al^{3+} and SO_4^{2-} ions. Hence in these salts the individual ions do not lose their identity. Such compounds are called *double salts* or *lattice compounds*. On the other hand, if solutions of $\text{Fe}(\text{CN})_2$ and KCN are mixed together and evaporated, potassium ferrocyanide $\text{Fe}(\text{CN})_2 \cdot 4\text{KCN}$ is formed. The aqueous solution of this salt does not give the test of Fe^{2+} ions and CN^- ions but gives the test for K^+ and ferrocyanide ion, $\text{Fe}(\text{CN})_6^{4-}$.



Thus we see that in the above compound the individual ions lose their identity. Such compounds are termed as coordination compounds or complex compounds. Their aqueous solution does not contain simple ions; instead the complex ion remains intact. A coordination compound may consist of a

- Simple cation and complex anion, for example, $\text{K}_4[\text{Fe}(\text{CN})_6]$
- Complex cation and simple anion $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3$
- Complex cation and complex anion, for example, $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$.

The ions $[\text{Fe}(\text{CN})_6]^{2-}$, $[\text{Pt}(\text{NH}_3)_5\text{Cl}]^{4+}$, $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$ are the complex ions. A complex ion is an electrically charged radical formed by the union of a metal cation with one or more neutral molecules or anions.

20.2 Terms Used in Coordination Chemistry

1. **Ligand:** A ligand is an atom, ion or molecule capable of donating an electron pair to the central metal atom. It may be a neutral molecule, negatively charged ion and can even be positively charged ion like nitrosylium ion. Generally ligands are electron pair donor but in metal carbonyls the ligand CO acts both as donor and acceptor.

Classification of ligands:

- a. **Monodentate or unidentate ligands:** These ligands have only one donor atom and hence coordinate to the central atom at one site only. They may be neutral like H_2O , NH_3 , CO , negatively charged like F^- , Br^- , CN^- , CH_3COO^- or positively charged like NO^+ , NH_2NH_3^+ .
- b. **Polydentate ligands:** These are ligands having more than one donor atom which may simultaneously coordinate to central atom at several sites. Ligands with two donor atoms are termed as bidentate ligands, for example, ethylenediamine $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ having

two neutral donor atoms (N atoms), oxalate ion $\left[\begin{array}{c} \text{O}=\text{C}-\text{O} \\ | \\ \text{O}=\text{C}-\text{O} \end{array} \right]^{2-}$ with two acidic (anionic)

donors and glycinate ion $\text{NH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}^-$ with a neutral donor (N atom) and an

acidic donor viz O^-

Similarly, ligands with three, four, five and six donor atoms are termed as tridentate, tetradentate, pentadentate and hexadentate ligands, respectively. EDTA is the most commonly known hexadentate ligand capable of donating six pairs of electrons to the central metal atom.

2. **Central ion:** It is the cation which accepts the electron pair, for example, in the complex $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, Cu^{2+} is the central ion.
3. **Coordination Number or Ligancy:** It is the total number of atoms of the ligand that can coordinate to the central metal ion. Coordination number represents the number of chemical bonds formed between the central metal ion and the donor atoms of the ligands.

Complex ion	Ligand	Coordination number
(i) $[\text{Fe}(\text{CN})_6]^{3-}$	CN	6
(ii) $[\text{Ni}(\text{CO})_4]$	CO	4
(iii) $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	6
(iv) $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$	H_2O and NH_3	6

4. **Coordination sphere:** The central metal atom and the ligands attached directly to it are enclosed in square brackets. This is collectively termed as the coordination sphere and it behaves as a single constituent unit. In $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Fe}(\text{CN})_6]^{4-}$ constitutes the coordination sphere.
5. **Charge on complex ion:** It is the algebraic sum of the charges carried by the central ion and the ligands attached to it, for example, in the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$, ferrous ion carries a charge of +2 and the six cyanide ions carry a charge of -6, hence the net charge on the complex ion is -4. Similarly, $[\text{Ag}(\text{CN})_2]^-$ has a net charge of -1 as Ag carries a charge of +1 and the two cyanide ions carry a charge of -2.

6. *Oxidation number:* It is the charge on the central atom in the coordination compound, for example, the oxidation number of Fe in $\text{Fe}(\text{CN})_6^{4-}$ is +2 and that of Co in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is +3 as NH_3 is neutral.

20.3 Nomenclature of Coordination Compounds

The general rules laid down by IUPAC for naming coordination compounds are as follows:

1. While naming a coordination compound the positive ion (cation) is named first followed by the negative ion (anion), for example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$ potassium is named first followed by the complex ion. Similarly in $[\text{Co}(\text{NH}_3)_5]\text{Cl}_3$ the cation $[\text{Co}(\text{NH}_3)_5]^{3+}$ is named before the anion Cl^- .
2. *Naming of coordination sphere* While naming the coordination sphere, the ligands are named first followed by the central metal ion. The ligands are written in alphabetical order regardless of the charge on them. For example, in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$, ammonia is written before chloride, followed by the metal. If the complex ion contains more than one metal atom then it is indicated by using the prefixes di, tri and so on; for example, $[\text{Re}_2\text{Cl}_8]^{2-}$ is named as octachloridodirhenate(III).
3. *Naming of ligands*
 - (i) *Negative ligands* (end in o) The names of negative ligands ending in 'ide', 'ite' and 'ate' respectively, are changed to end in 'ido', 'ito' and 'ato', respectively. Certain simple ligands which were earlier represented as fluoro, chloro, bromo, iodo, hydroxo, cyano, oxo, etc. are now fluoro, chlorido, bromido, hydroxido, hydrido, cyanido, oxido, etc. (IUPAC recommendations for inorganic nomenclature 2005).
 - (ii) *Positive ligands* (end in -ium) :
 - NO^+ nitrosonium
 - NO^{2+} nitronium
 - NH_2NH_3^+ hydrazinium
 - (iii) *Neutral ligands* (named as such)
 - $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ethylenediamine
 - $\text{C}_5\text{H}_5\text{N}$ pyridine
 - $(\text{C}_6\text{H}_5)_3\text{P}$ triphenylphosphine

However, there are several exceptions in naming neutral ligands. For example

 - H_2O aqua
 - NH_3 ammine
 - NO nitrosyl
 - CO carbonyl
 - O_2 dioxygen
 - N_2 dinitrogen

The names of ligands in accordance with IUPAC recommendations 2005 are given in Table 20.1.

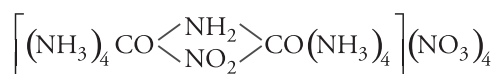
4. *Order of naming ligands* In case of the coordination sphere consisting of more than one ligand, then the ligands are named in alphabetical order (ignoring numerical prefixes) without separation by hyphen irrespective of the charge on them, for example, $[\text{Co}(\text{NH}_3)_4\text{Cl}(\text{NO}_2)]^+$ the ligands are named in the order ammine, chlorido and nitro. Similarly in the complex $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$ the ligands are named in the order cyanido followed by nitrosyl.
5. *Indicating the number of ligands* Two, three, four, five and six ligands are represented by using the prefixes di, tri, tetra, penta and hexa, respectively. If the ligand itself includes the prefix di, tri and tetra, then the prefix bis, tris and tetrakis are used for two, three and four ligands with the ligand name in parentheses. For example, two ethylenediamine will be represented as bis(ethylenediamine).
6. *Indicating central metal atom* For cationic and neutral complexes, the central metal ion is written as such but for anionic complexes 'ate' is suffixed to the name of the metal, for example,

$\text{K}[\text{Pt}(\text{NH}_3)_5\text{Cl}_5]$ potassium amminepentachloridoplatinate(IV).

For anionic complexes, the Latin names of the metals are generally used

Fe	Ferrate	Sn	Stannate
Au	Aurate	Ag	Argentate
Cu	Cuprate		

7. *Oxidation number of the central metal atom* The ligand name is followed by the name of central metal atom with the oxidation number in parentheses in roman numerals following the metal atom without a gap between the two as in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ pentaamminechloridocobalt(III) chloride (The roman numeral III in parentheses indicates the oxidation number of cobalt) or the overall charge on the complex written in parentheses as pentamminecobalt(2+)chloride.
8. *Bridging ligands* Bridging ligands are preceded by the Greek letter μ (mu), which is repeated before the name of each different kind of bridging group, for example,



μ -amido - μ -nitrobis(tetraamminecobalt(III) nitrate).

In case of ambidentate ligands, which have more than one donor atom, the letter κ is used to indicate the atom of ligation. For example if the thiocyanato ion coordinates with the metal ion through N atom $(\text{NCS})^-$ it is written as thiocyanato - κN and if it coordinates through the S atom it is expressed as thiocyanato - κS . Similarly NO_2^- is written as nitrito - κN for ligation through N atom as in $\text{M} - \text{NO}_2^-$ and as nitrito - κO for ligation through O atom as in $\text{M} - \text{ONO}^-$.

$[\text{Zn}(\text{NCS})_4]^{2+}$ tetrathiocyanato - κN - zinc(II) since the ligand is attached to central metal atom through N atom.

Note: the κ terminology has only been recently introduced. Earlier coordination through N was indicated by isothiocyanato and coordination through S was indicated by thiocyanato. However, the old terminology is still widely used.

The above-mentioned rules are further illustrated by the examples given below.

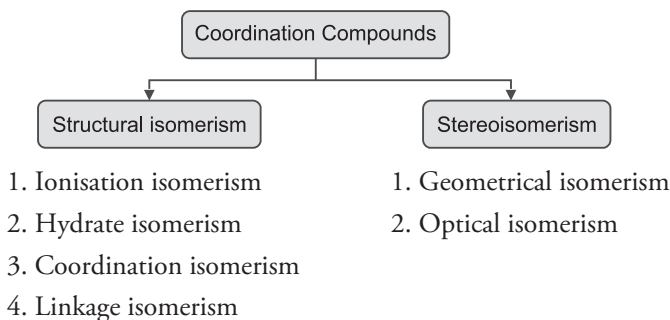
1. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ hexaamminecobalt(III)chloride
2. $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ pentaamminechloridocobalt(III)
3. $[\text{CoCl. CN. NO}_2(\text{NH}_3)_3]$ triamminechloridocyanidonitrito- κN -cobalt(III)
4. $[\text{Cd}(\text{SCN})_4]^{2+}$ tetrathiocyanato- κS -cadmium(II)
5. $\text{K}_4[\text{Fe}(\text{CN})_6]$ potassium hexacyanidoferrate(II)
6. $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$ potassium pentacyanidonitrosylferrate(II)
7. $\text{Fe}(\text{C}_5\text{H}_5)_2$ bis(cyclopentadienyl)iron(II)
8. $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$ tetrapyridineplatinum(II)tetrachloridoplatinate(II)
9. $[\text{Cr}(\text{en})_3]\text{Cl}_3$ tris(ethylenediamine)chromium(III)chloride
10. $[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$ dichloridobis(methylamine)copper(II)

Table 20.1 Common ligands and their names

Formula	Ligand name
Cl^-	Chlorido
Br^-	Bromido
CN^-	Cyanido
H^-	Hydrido
F^-	Fluorido
OH^-	Hydroxido
I^-	Iodido
NO_3^-	Nitrato
O^{2-}	Oxido
S^{2-}	Sulphido
CO_3^{2-}	Carbanato
NO_2^-	Nitrito- κN
ONO^-	Nitrito- κO
NCS^-	Thiocyanato- κN
SCN^-	Thiocyanato- κS
H_2O	Aqua
NH_3	Ammine
CO	Carbonyl
C_5H_5^-	Cyclopentadienyl
$\text{C}_5\text{H}_5\text{N}$	Pyridine
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	Ethylenediamine
$\text{C}_2\text{O}_4^{2-}$	Oxalato
$\text{H}_2\text{NCH}_2\text{COO}^-$	Glycinato

20.4 Isomerism in Coordination Compounds

Isomerism is the phenomenon where the compounds have the same molecular formula but different structural arrangements. The two compounds exhibiting the above-mentioned phenomenon are called isomers. Isomerism shown by coordination compounds is summarised as follows:

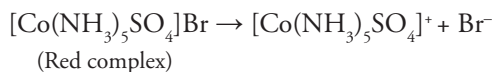
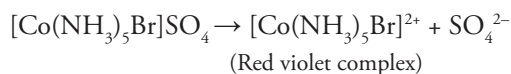


Let us discuss different types of isomerisms.

A. Structural isomerism (now termed as constitutional isomerism)

1. *Ionisation isomerism*: These are isomers that yield different ions in solution. This is due to the exchange of groups inside the coordination sphere and outside it. This type of isomerism is well illustrated by the complex with formula $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$. It exhibits two types of isomers:

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is red violet and its aqueous solution gives white precipitate of BaSO_4 with BaCl_2 solution confirming the presence of free SO_4^{2-} ions in solution.
- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ is red and does not give the test of sulphate ions instead gives cream coloured precipitate of AgBr with AgNO_3 , thereby confirming the presence of Br^- ions.



Other complexes exhibiting ionisation isomerism are

- (a) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
 - (b) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{NO}_2$ and $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{Cl}$
 - (c) $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{SCN}$ and $[\text{Co}(\text{en})_2(\text{NO}_2)\text{SCN}]\text{Cl}$
2. *Hydrate isomerism*: It is similar to ionisation isomerism, difference being that here the number of water molecules inside and outside the coordination sphere vary. The compound with molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ has three isomers:

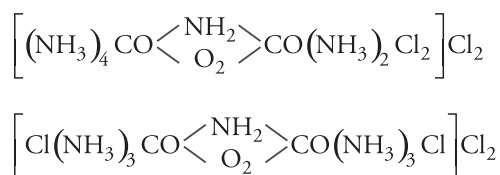
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ violet with three ionic chlorines

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ green with two ionic chlorines

$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ dark green with one ionic chlorine

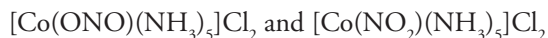
Other examples of hydrate isomerism are

- (a) $[\text{CoCl}(\text{en})_2(\text{H}_2\text{O})]\text{Cl}_2$ and $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$
 - (b) $[\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl} \cdot \text{H}_2\text{O}$
 - (c) $[\text{CrCl}_2(\text{py})_2(\text{H}_2\text{O})_2]\text{Cl}$ and $[\text{CrCl}_3(\text{py})_2(\text{H}_2\text{O})]\text{H}_2\text{O}$
3. *Coordination isomerism*: Coordination compounds with complex cation and anion exhibit this type of isomerism. It occurs due to interchange between the cationic and anionic parts. Common examples of coordination isomerism are
- (a) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
 - (b) $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{PtCl}(\text{NH}_3)_3][\text{PtCl}_3(\text{NH}_3)]$
 - (c) $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{CN})_2(\text{NH}_3)_4][\text{Cr}(\text{CN})_4(\text{NH}_3)_2]$
 - (d) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
4. *Coordination position isomerism*: It is a special case of coordination isomerism that occurs in polynuclear or bridged complexes due to exchange of ligands between different metal nuclei. For example



5. *Linkage isomerism*: This type of isomerism is shown by ligands having two different donor atoms (ambidentate ligands). Such ligands can coordinate with the central metal atom with either of the donor atom giving rise to linkage isomerism. For example, NO_2 can coordinate with the central metal atom either through N atom as donor or with O atom as donor.
- (a) NO_2^- ion Nitro bonding occurs through N
 ONO^- Nitrito bonding occurs through O
 - (b) CN^- cyanido bonding occurs through C
 NC^- isocyanido bonding occurs through N
 - (c) SCN^- thiocyanato bonding occurs through S
 NCS^- isothiocyanato bonding occurs through N

An example of linkage isomerism is



B. Stereoisomerism

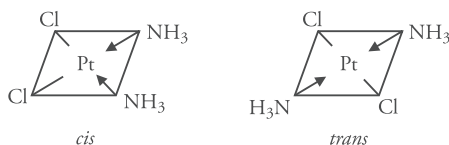
1. *Geometrical isomerism*: Disubstituted complexes having coordination numbers 4 and 6 show geometrical isomerism. Two types of geometrical isomers exist – when the identical groups are adjacent to each other, the isomer is a *cis* isomer and when they are opposite to each other the isomer is a *trans* isomer.

Geometrical isomerism in compounds with coordination number 4:

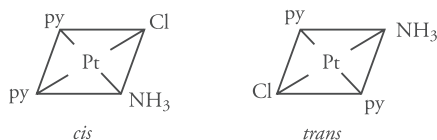
Tetrahedral compounds and square planar complexes of the type Ma_4 , Ma_3b or Mab_3 do not exhibit geometrical isomerism. Complexes of the type Ma_2b_2 , Mabx_2 or Mabxy show geometrical isomerism.

Let us consider some examples

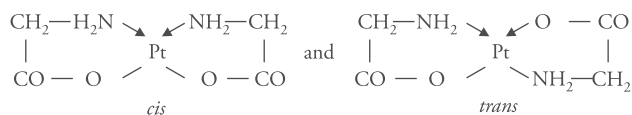
- (i) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ exists in *cis* and *trans* forms as



- (ii) $[\text{PtCl}(\text{py})_2(\text{NH}_3)]$



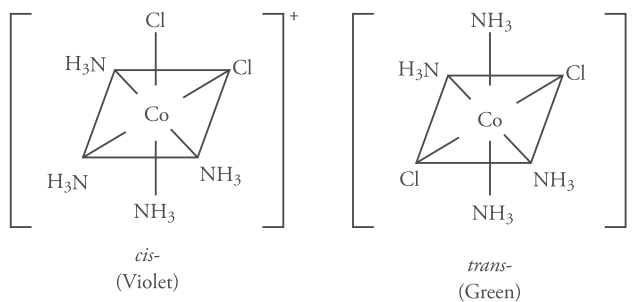
- (iii) Similarly a complex with an unsymmetrical bidentate ligand also exhibits *cis trans* isomerism



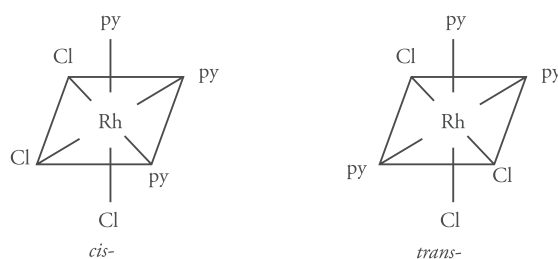
Geometrical isomerism in compounds with coordination number 6

Octahedral complexes of the types Ma_6 , Ma_5b and Mab_5 do not exhibit geometrical isomerism.

- (i) Ma_4b_2 type complexes : Example $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

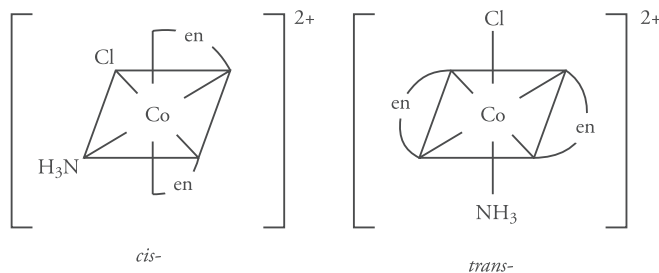
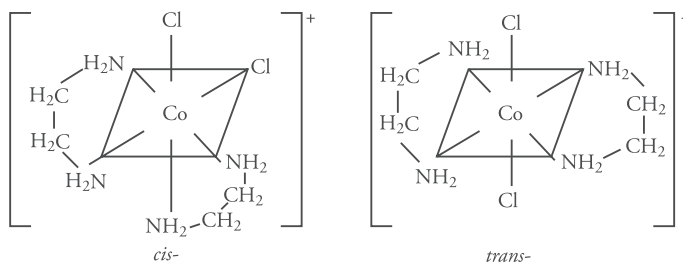


(ii) Ma_3b_3 type complexes. Example: $[\text{Rh}(\text{py})_3\text{Cl}_3]$



(ii) Complexes of the type Mabcdef also exhibit geometrical isomerism. The only known example of this type is $[\text{Pt}(\text{py})(\text{NH}_3)(\text{NO}_2)(\text{Cl})(\text{Br})(\text{I})]$

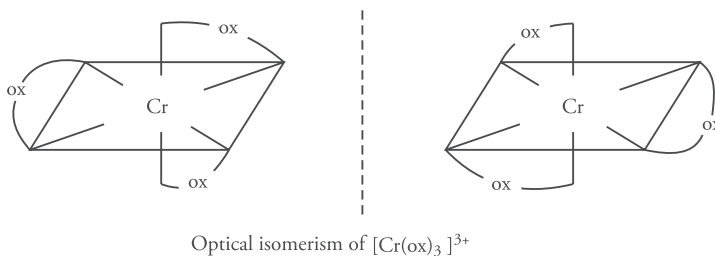
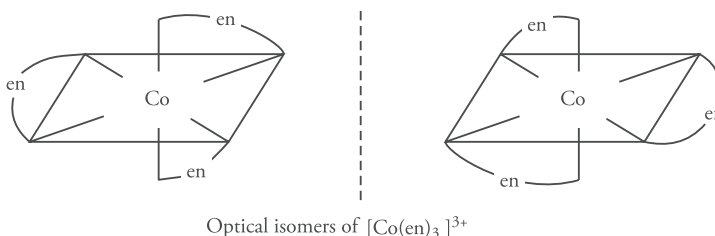
(iii) $\text{M}(\text{aa})_2\text{b}_2$ and $\text{M}(\text{aa})_2\text{xy}$ type complexes. Example: $[\text{CoCl}_2(\text{en})_2]^+$



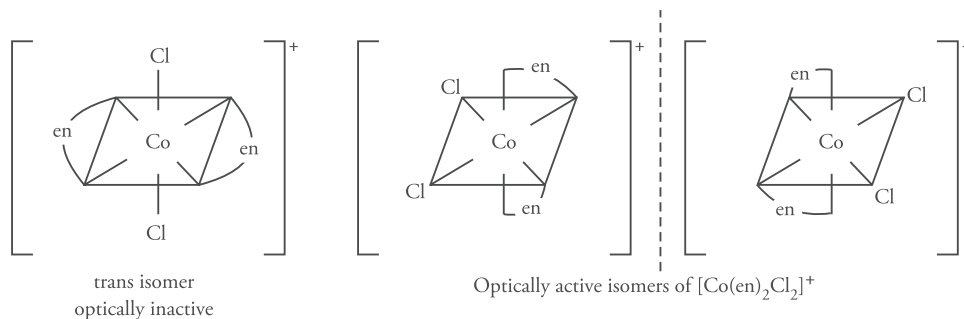
Optical isomerism: Like organic compounds coordination compounds also exhibit optical isomerism, that is, they can rotate the plane of polarised light. Coordination compounds which lack plane of symmetry and form non-superimposable mirror image are optically active. Isomers that rotate the plane of polarised light to the right are called *dextrorotatory* and those that rotate the plane of polarised light to the left are termed as *laevorotatory*. *Racemic mixture* is an optically inactive mixture of both these isomers in the ratio 1:1. The isomers rotating the plane of polarised light equally but in opposite directions are called *enantiomers or enantiomorphs*. Some examples of coordination compounds showing optical isomerism are discussed below:

- (i) Octahedral complexes of the type $[M(AA)_3]$ where AA is a symmetrical bidentate ligand.

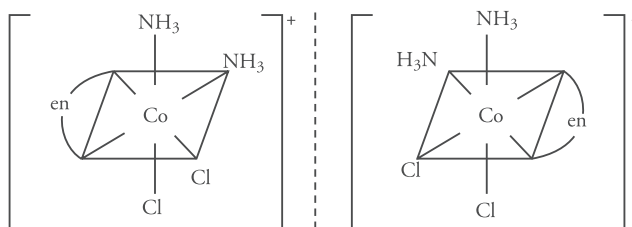
Example: $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{ox})_3]^{3+}$



- (ii) Complexes of the type $[M(AA)_2X_2]$ and $[M(AA)_2XY]$ where AA is again a symmetrical bidentate ligand. Examples: $[\text{CoCl}_2(\text{en})_2]^+$, $[\text{RhCl}_2(\text{en})_2]^+$, $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^{2+}$, $[\text{Ru}(\text{py})(\text{C}_2\text{O}_4)(\text{NO})]$

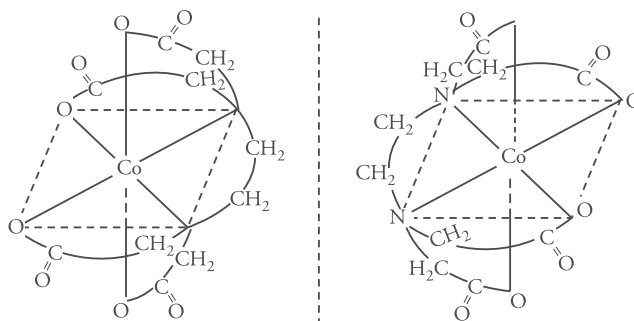


- (iii) Complexes of the type $[M(AA)X_2Y_2]$ exist in two optically active and one optically inactive form. Example: $[\text{Co}(\text{en})(\text{NH}_3)_2(\text{Cl})_2]^+$ and $[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_2(\text{NO}_2)_2]^-$



Optical isomers of $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$

- (iv) Complexes containing polydentate ligands. Example: $[\text{Co}(\text{EDTA})]^-$



20.5 Bonding in Coordination Compounds: Werner's Coordination Theory

The first attempt to explain bonding in coordination compounds was made by Alfred Werner in 1893. His painstaking work of twenty years in this field won him the Nobel prize for chemistry in 1913. The main postulates of his theory are:

- (i) In a coordination complex a metal shows two types of valencies
 - *Primary valency or ionizable valency:* This is ionizable, non-directional valency and corresponds to the oxidation state of the metal ion. It is satisfied by negative ions both in simple salts and complex salts. For example in a simple salt CuSO_4 , the primary valency of copper is two, that is, copper forms two ionic bonds. Similarly in the complex $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ which ionises as $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and SO_4^{2-} ; copper again has a primary valency of two as this compound also has two ionic bonds.
 - *Secondary or non-ionizable valency:* This is directional, non-ionizable valency and it corresponds to the coordination number of the metal ion under consideration. Secondary valency equals the number of ligand atoms coordinated to the central metal ion. A metal complex first satisfies its coordination valency and then its primary valency.

Secondary valency being directional imparts a definite geometry to the complex. It may be satisfied by negative ions, neutral molecules or sometimes even by positive ions.

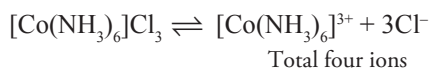
Experimental evidence in support of Werner's theory

Werner prepared six compounds of cobalt(III)chloride with ammonia.

- (ii) $\text{CoCl}_3 \cdot 6\text{NH}_3$: It is an orange-yellow compound. On adding AgNO_3 to the solution of this compound, all three chloride ions precipitate showing that they constitute the primary valency or ionizable valency. Conductance measurements indicate the presence of four ions in the complex. From the above considerations, Werner formulated the formula of this complex as

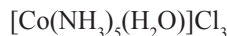


Hence cobalt has a secondary valency of six and primary valency of three. It ionises as

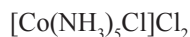


The three chloride ions are precipitated by adding AgNO_3 .

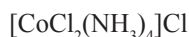
- (iii) $\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$: It is a pink crystalline solid. On adding AgNO_3 , three chloride ions precipitate and conductance measurements reveal the presence of four ions. Werner formulated the complex as



- (iv) $\text{CoCl}_3 \cdot 5\text{NH}_3$: It is a violet coloured compound. Addition of AgNO_3 leads to precipitation of two chloride ions, and conductance measurements show the presence of three ions. Hence the formula was written as



- (v) One chloride enters the coordination sphere to satisfy the secondary valency. (iv and v) $\text{CoCl}_3 \cdot 4\text{NH}_3$: Two compounds of the same composition, one violet and the other green, have been prepared. The conductance studies show the presence of only two ions and only one chloride is precipitated on adding AgNO_3 . Hence the structure was written as

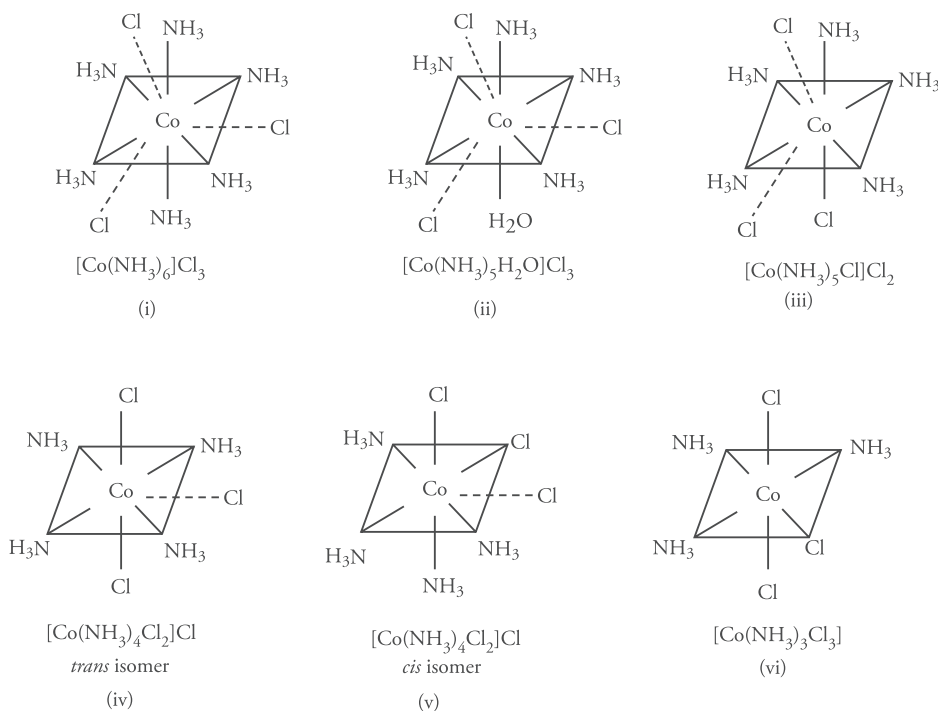


Werner explained these two compounds of same composition by assuming that one is *trans* isomer and the other is a *cis* isomer.

- (vi) $\text{CoCl}_3 \cdot 3\text{NH}_3$: It is blue-green coloured compound which does not conduct electricity, marking the absence of any ions in solution. Hence in this compound all the chloride ions are linked to the central metal atom constituting the unionizable secondary valency. This is further validated by the fact that this compound does not give a precipitate with AgNO_3 solution. Hence its formula was given by Werner as



Since the secondary valency or coordination number of these compounds is 6, they acquire octahedral geometry.



Structures of cobalt (III) ammine complexes

20.6 Sidgwick Coordination Theory

Professor N. V. Sidgwick of Oxford University explained bonding in coordination compounds on the basis of the lewis concept. He postulated that the ligands act as electron pair donor and the central metal atom is the electron pair acceptor. There exists a coordinate bond between the two. He suggested that the total number of electrons around the central metal atom is equal to the atomic number of the next noble gas. This is also known as the *effective atomic number* which is equal to the total electrons possessed by the central metal ion in the complex including those gained from the ligands by coordinate bond. Consider the example of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. Cobalt has an atomic number of 27, so the central metal ion Co^{3+} has 24 electrons. The addition of six electron pairs from ligand NH_3 adds 12 electrons. Hence the effective atomic number (EAN) of cobalt becomes $24 + 12 = 36$ which corresponds to the atomic number of next noble gas, krypton. Hence according to Sidgwick this complex will be stable. Table 20.2 gives the EAN for other complexes. However, as shown in Table 20.3, not all stable complexes follow the EAN rule, which shows that tendency to attain noble gas configuration is an important factor but not a necessary condition for complex formation.

Table 20.2 Complexes that follow EAN rule

Complex	Central metal ion	Atomic number of central metal ion	Electrons on metal ion	Electrons gained by coordination	EAN	Atomic number of next noble gas
$[\text{Fe}(\text{CN})_6]^{4-}$	Fe^{2+}	26	$26 - 2 = 24$	$6 \times 2 = 12$	36	36 (Kr)
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Co^{3+}	27	$27 - 3 = 24$	$6 \times 2 = 12$	36	36 (Kr)
$[\text{Ni}(\text{CO})_4]$	Ni	28	$28 - 0 = 28$	$4 \times 2 = 8$	36	36 (Kr)
$[\text{Cu}(\text{CN})_4]^{3-}$	Cu^+	29	$29 - 1 = 28$	$4 \times 2 = 8$	36	36 (Kr)
$[\text{Pd}(\text{NH}_3)_6]^{4+}$	Pd^{4+}	46	$46 - 4 = 42$	$6 \times 2 = 12$	54	54 (Xe)
$[\text{Cd}(\text{NH}_3)_4]^{2+}$	Cd^{2+}	48	$48 - 2 = 46$	$4 \times 2 = 8$	54	54 (Xe)
$[\text{Pt}(\text{NH}_3)_6]^{4+}$	Pt^{4+}	78	$78 - 4 = 74$	$6 \times 2 = 12$	86	86 (Rn)
$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$	Pt^{4+}	78	$78 - 4 = 74$	$6 \times 2 = 12$	86	86 (Rn)

Table 20.3 Complexes that do not follow EAN rule

Complex	Central metal ion	Atomic number of central metal ion	Electrons on metal ion	Electrons gained by coordination	EAN	Atomic number of nearest noble gas
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	Cr^{3+}	24	$24 - 3 = 21$	$6 \times 2 = 12$	33	36 (Kr)
$[\text{Ni}(\text{en})_3]^{2+}$	Ni^{2+}	28	$28 - 2 = 26$	$6 \times 2 = 12$	38	36 (Kr)
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Ni^{2+}	28	$28 - 2 = 26$	$6 \times 2 = 12$	38	36 (Kr)
$[\text{CuCl}_2]^-$	Cu^+	29	$29 - 1 = 28$	$2 \times 2 = 4$	32	36 (Kr)
$[\text{Ag}(\text{NH}_3)_2]^+$	Ag^+	47	$47 - 1 = 46$	$2 \times 2 = 4$	50	54 (Xe)
$[\text{Pt}(\text{NH}_3)_4]^{2+}$	Pt^{2+}	78	$78 - 2 = 76$	$4 \times 2 = 8$	84	86 (Rn)

20.7 Valence Bond Theory

This theory based on the concept of hybridisation was given by Linus Pauling. The main postulates of the theory are as follows:

- The ligand donates an electron pair to the central metal ion through coordinate bond.
- The central metal ion makes empty orbitals available to accommodate these electrons. The number of empty orbitals required is equal to the coordination number of the metal ion. If the coordination number is six, then six vacant orbitals are required and if it is four then four vacant orbitals will be required.
- The central metal ion contains s, p, d orbitals, all of which are of different energies and orientations. These atomic orbitals hybridise to form equal number of hybrid orbitals that are equivalent in energy and symmetry and form bonds with the ligands.
- The ligands approach the central metal ion and donate electron pairs to vacant hybridised orbitals of the metals. A ligand–metal coordinate bond is formed by the overlap of empty hybridised orbitals of metal ions and filled ligand orbitals. Depending upon the atomic orbitals involved in hybridisation the complexes can acquire different geometries as given in Table 20.4.

Table 20.4 Hybridisation and geometries of some complexes

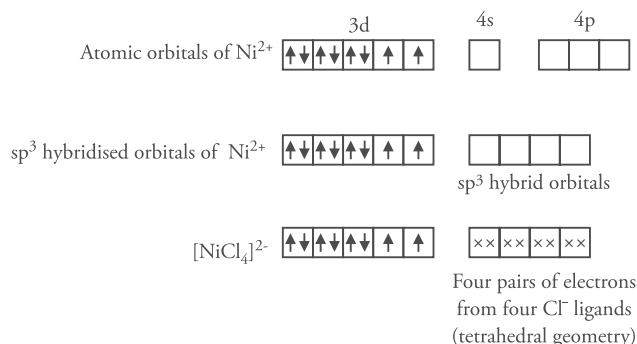
Coordination number	Type of hybridisation	Geometry	Examples
4	sp^3	Tetrahedral	$[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{CO})_4]$
4	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_4]^{2-}$
6	d^2sp^3 or sp^3d^2	Octahedral	$[\text{Cr}(\text{NH}_3)_6]^{2+}$, $[\text{Fe}(\text{CN})_6]^{3-}$

- (v) The d orbitals involved in hybridisation may be inner d orbitals (n-1) or outer d orbitals. Accordingly the complexes formed are inner orbital (low spin or spin paired) complexes or outer orbital (high spin or spin free) complexes.
- (vi) A complex is paramagnetic if it contains unpaired electrons and diamagnetic if all its electrons are paired.

The following examples illustrate the application of valence bond theory in the formation of some complexes.

Coordination number 4

- (i) *Bonding in $[\text{NiCl}_4]^{2-}$* : In $[\text{NiCl}_4]^{2-}$, nickel is in +2 oxidation state and has $3d^84s^0$ configuration. It has two unpaired electrons. The complex is paramagnetic with magnetic moment corresponding to two unpaired electrons. To accommodate four electron pairs of Cl^- ion, nickel makes available one 4s and three 4p orbitals for hybridisation. This is shown in Figure 20.1

**Figure 20.1** Bonding in $[\text{NiCl}_4]^{2-}$

2. *Bonding in $[\text{Ni}(\text{CO})_4]$* : $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry, but here the oxidation state of Ni is zero. Its outer electronic configuration is $3d^84s^2$. Since CO is a strong field ligand (strong and weak field ligands are discussed later), it forces the 4s electrons to pair up with the electrons of the 3d orbitals, thus vacating the 4s orbital. Now one 4s and three 4p orbitals

undergo hybridisation to form sp^3 complex, which is diamagnetic due to the absence of unpaired electrons.

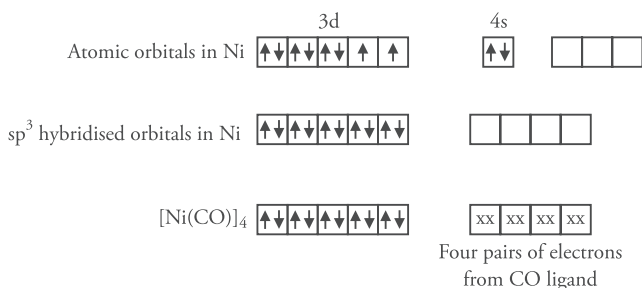


Figure 20.2 Bonding in $[Ni(CO)_4]$

3. **Bonding in $[Ni(CN)_4]^{2-}$:** It is a square planar complex, where nickel is in +2 oxidation state with electronic configuration $3d^8 4s^0$. Since CN^- is a strong field ligand it forces the two unpaired d electrons to pair up and leave a vacant d orbital. One 3d orbital, one 4s orbital and two 4p orbitals undergo hybridisation giving four dsp^2 hybrid orbitals that accommodate the four electron pairs of CN^- ligands. Since the complex has no unpaired electron it is diamagnetic. The bonding scheme is as follows:

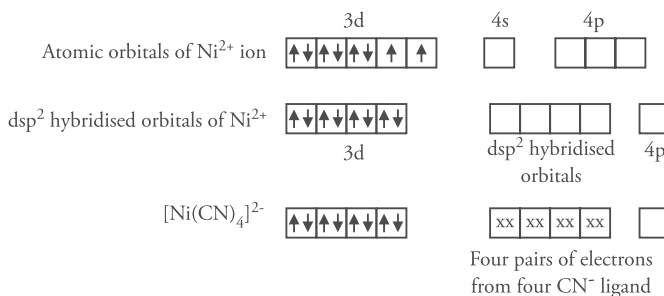


Figure 20.3 Bonding scheme in $[Ni(CN)_4]^{2-}$

Coordination number 6

1. **Bonding in $[Co(NH_3)_6]^{3+}$:** The central metal atom, cobalt is in +3 oxidation state with four unpaired electrons. However, the complex is diamagnetic showing the absence of unpaired electrons. Hence VBT states that during complex formation the electrons in the d orbitals pair up and two vacant d orbitals are made available. Two inner vacant 3d orbitals, one 4s orbital and three 4p orbitals undergo hybridisation to form six d^2sp^3 hybrid orbitals which accommodate the six electron pairs from NH_3 ligands. The bonding scheme is as follows:

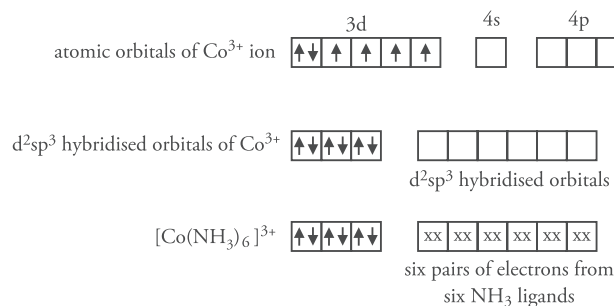


Figure 20.4 Bonding scheme in $[\text{Co}(\text{NH}_3)_6]^{3+}$

Since this complex uses inner d orbitals for hybridisation they are called *inner orbital* or *low spin* or *spin paired complex*.

2. *Bonding in $[\text{CoF}_6]^{3-}$* : Like $[\text{Co}(\text{NH}_3)_6]^{3+}$, in $[\text{CoF}_6]^{3-}$ also cobalt exists in +3 oxidation state having four unpaired electrons in its atomic orbitals. But here the complex is octahedral and paramagnetic with magnetic moment corresponding to four unpaired electrons. Hence the hybridisation is explained using the outer d orbitals. These complexes are termed as *outer orbital* or *high spin* or *spin free complexes*.

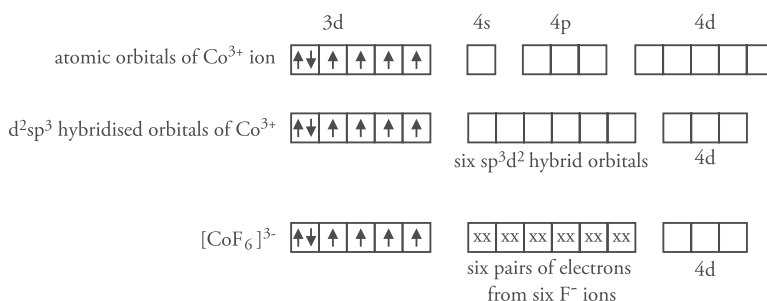


Figure 20.5 Bonding scheme in $[\text{CoF}_6]^{3-}$

Limitations of Valence Bond Theory

1. The representation of bonding given by valence bond theory is essentially qualitative in nature. It offers no explanation to the electronic spectra and colour of coordination compounds, their stabilities, reactivities or mechanism of reactions.
2. Valence bond theory considers that the magnetic moments of complexes is due to the magnetic field generated by the spin of electrons. It does not take into account the orbital motion of electrons. This is the reason why the experimental values differ from those predicted on the basis of valence bond theory. The correct magnetic moment is the sum of μ_{spin} and μ_{orbital} .
3. According to valence bond theory the square planar complexes of $\text{Cu}(\text{II})$ as in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ have dsp^2 hybridisation in which the d orbital is vacated by the promotion of unpaired 3d

electron to $4p_z$ orbital. According to this explanation the square Cu(II) complexes should easily oxidise to Cu(III) complexes because removal of electron from $4p_z$ orbital would be easy. But the oxidation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to $[\text{Cu}(\text{NH}_3)_4]^{3+}$ does not occur at all.

4. VBT fails to explain why a metal forms inner orbital complexes and at other times it forms outer orbital complexes. For instance, $[\text{Co}(\text{NH}_3)_4]^{3+}$ is diamagnetic and an inner orbital complex, whereas $[\text{CoF}_6]^{3-}$ is paramagnetic and an outer orbital complex.
5. Octahedral complexes (d^2sp^3 or sp^3d^2 hybridisation), tetrahedral (sp^3) or square planar (dsp^2 hybridisation) of complexes of d^1 , d^2 , d^3 and d^9 ions have the same number of unpaired electrons, hence merely on the basis of unpaired electrons it is difficult to predict the geometry and hybridisation of these complexes.
6. VBT lays too much stress on central metal ion and the role of ligand is not properly emphasised.

20.8 Crystal Field Theory

This theory was originally put forward by Brethe and van Vleck in 1930s and later popularised for inorganic chemists by Orgel in the 1950s. It applied mainly to ionic crystals, hence is termed as the crystal field theory. The main postulates of the theory are as follows:

1. A complex is considered as a combination of central metal ion surrounded by ligands.
2. The interaction between metal ion and ligands is purely ionic due to electrostatic interaction between the metal ions and ligands; both being assumed to be point charges.
3. Ligands are regarded as point charges. Ionic ligands like F^- , Cl^- , CN^- , etc are regarded as negative point charges and neutral ligands like H_2O and NH_3 are regarded as dipoles such that they approach the central metal ion with negative poles towards the central metal ion.
4. All the d orbitals on the metal atom have equal energy (degenerate orbitals). As the ligands approach the central metal atom for complex formation, these orbitals lose their degeneracy and split into orbitals of different energies depending upon the direction from which the ligands approach the central metal atom.
5. Unlike valence bond theory, this theory does not consider covalent character of bond between metal and ligand. The metal ions and ligand do not mix their orbitals or share electrons, that is it does not consider any type of orbital overlap.

Crystal field splitting of d orbitals

In an isolated gaseous ion all the five d orbitals are degenerate i.e., they have the same energy. On approach of ligands, the electrons in the d orbitals of the central metal ion are repelled by the electron pair of the ligands. This repulsion raises the energy of the d orbitals and if the field of negative charges is spherically symmetrical, the d orbitals still remain degenerate but with higher energy.

In reality the field produced by ligands is not spherically symmetrical as the d orbitals differ in orientation. The d_{z^2} and $d_{x^2-y^2}$ orbitals have their lobes along the axes and are called axial orbitals (group theory calls them e_g orbitals where e refers to doubly degenerate) whereas the lobes of d_{xy} ,

d_{yz} and d_{xz} lie in between the x, y and z axes and hence they are termed as the non-axial orbitals (group theory terms them as t_{2g} orbitals, where t refers to triply degenerate set).

The energy of orbitals lying in the direction of approach of ligands rises to a greater extent than that of the orbitals lying in between them. Hence under the influence of ligands the five degenerate d orbitals split into two sets of orbitals having different energies. This splitting of d orbitals is termed as crystal field splitting or energy level splitting. Let us discuss splitting in octahedral, tetrahedral and square planar complexes.

(A) Splitting of d orbitals in octahedral complexes

In octahedral complexes the ligands approach central metal atom along the axis, as a result of which the axial orbitals (d_z^2 and $d_{x^2-y^2}$) experience greater repulsion than the non-axial orbitals (d_{xy} , d_{yz} and d_{xz}). Thus the degenerate d orbitals split into two degenerate sets, one consisting of lower energy and more stable d_{xy} , d_{yz} and d_{xz} orbitals (t_{2g} orbitals) and the other less stable higher energy d_z^2 and $d_{x^2-y^2}$ orbitals (e_g orbitals). This splitting of degenerate orbitals under the influence of ligands is termed as crystal field splitting and the energy separation between them is denoted by Δ_o or $10Dq$ (the subscript $_o$ stands for octahedral)

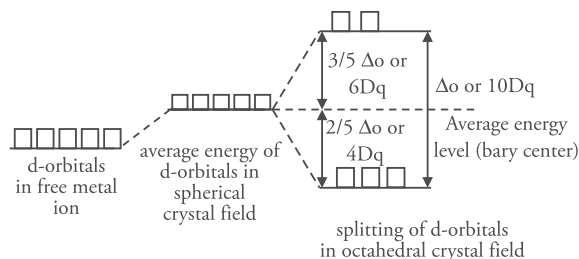


Figure 20.6 Splitting of d-orbitals in an octahedral crystal field

It has been found that the energy of the three t_{2g} orbitals decreases by $\frac{2}{5} \Delta_o$ or $0.4\Delta_o$ or $4Dq$ and the energy of e_g orbitals rises by $\frac{3}{5} \Delta_o$ or $0.6\Delta_o$ or $6Dq$ above the hypothetical degenerate d orbitals.

It is important to note that the crystal field splitting energy Δ_o depends upon the field produced by the ligand and the charge on the metal ion. Ligands that produce strong field and cause large splitting are called strong field ligands and those that produce weak field cause small degree of splitting and are termed as weak field ligands. The magnitude of Δ_o and hence the distribution of electrons in the d orbitals is influenced largely by the magnitude of the ligand field.

Based on experimental evidence the ligands are arranged in the order of increasing field strength in a series termed as the spectrochemical series.

Weak field ligands $I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < EtOH < \text{oxalate} < H_2O < NCS^- < EDTA^{4-} < (NH_3 \text{ and pyridine}) < en < \text{dipyridyl} < o\text{-phenanthroline} < NO_2^- < CN^- < CO$ Strong field ligand

Distribution of electrons in d orbitals: In the complexes with electronic configuration d^1 , d^2 and d^3 the electrons occupy the t_{2g} orbitals which are the lower energy orbitals in accordance with the

Hund's rule of maximum multiplicity. The energy of t_{2g} orbital with respect to the barycentre is $-0.4\Delta_o$ hence these configurations will be stabilised by $-0.4\Delta_o$ (d^1), $2 \times -0.4\Delta_o = -0.8\Delta_o$ (d^2), $3 \times -0.4\Delta_o = -1.2\Delta_o$ (d^3) respectively (negative sign shows that the energy is less than the energy of the bary centre). For d^4 electronic configuration there are two possibilities

1. Either the fourth electron occupies the t_{2g} orbital and pairs up with the existing electrons giving the configuration t_{2g}^4 or
2. It occupies the higher energy e_g orbital with electronic configuration $t_{2g}^3 e_g^1$.

If the electron enters the t_{2g} orbital, it experiences strong interelectronic repulsions and energy equal to pairing energy P is required to overcome them. Hence the net CFSE for t_{2g}^4 configuration will be $-1.6\Delta_o + P$. On the other hand if the electron enters the e_g orbital then pairing energy will not be required but e_g is at a higher energy. Hence the CFSE will be $-1.2\Delta_o + 0.6\Delta_o = -0.6\Delta_o$. Which configuration will be adopted depends on which energy, $-1.6\Delta_o + P$ or $-0.6\Delta_o$, is higher.

- (i) In case of weak field ligands $\Delta_o < P$, the fourth electron enters the e_g orbital and the configuration will be $t_{2g}^3 e_g^1$. Such complexes are termed as *high spin complexes* or *spin free complexes*.
- (ii) In case of strong field ligands $\Delta_o > P$ the fourth electron occupies the t_{2g} orbital to give the electronic configuration $t_{2g}^4 e_g^0$. Such complexes are termed as *low spin complexes* or *spin paired complexes*.

The above distribution of electrons can be illustrated by considering the example of $[\text{CoF}_6]^{3-}$, F^- being a weak field ligand and $[\text{Co}(\text{NH}_3)_6]^{3+}$, NH_3 being a strong field ligand.

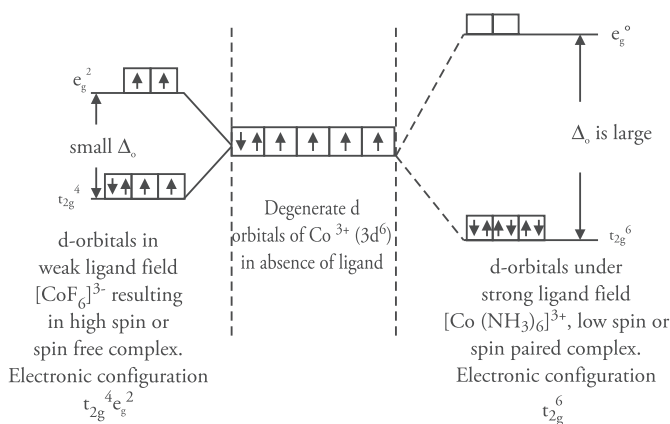


Figure 20.7 Electron distribution of $[\text{CoF}_6]^{3-}$ (weak field ligand) and $[\text{Co}(\text{NH}_3)_6]^{3+}$ (strong field ligand)

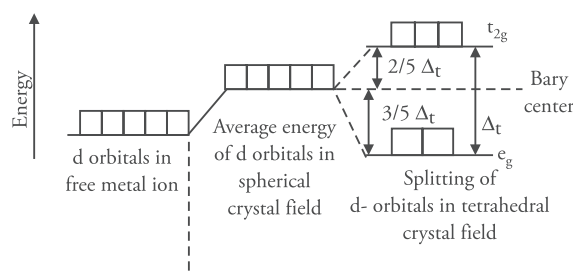
Table 20.5 shows the distribution of various d electrons of central metal cation in strong and weak octahedral ligand field.

Table 20.5 Distribution of d electrons of central metal cation in strong and weak octahedral ligand field

Number of d electrons	Strong field ligands (low spin or spin paired complexes) $\Delta_o > P$	Weak field ligands (high spin or spin free complexes) $\Delta_o < P$
d^1	$t_{2g}^1 e_g^0$	$t_{2g}^1 e_g^0$
d^2	$t_{2g}^2 e_g^0$	$t_{2g}^2 e_g^0$
d^3	$t_{2g}^3 e_g^0$	$t_{2g}^3 e_g^0$
d^4	$t_{2g}^4 e_g^0$	$t_{2g}^3 e_g^1$
d^5	$t_{2g}^5 e_g^0$	$t_{2g}^3 e_g^2$
d^6	$t_{2g}^6 e_g^0$	$t_{2g}^4 e_g^2$
d^7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$
d^8	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^2$
d^9	$t_{2g}^6 e_g^3$	$t_{2g}^6 e_g^3$
d^{10}	$t_{2g}^6 e_g^4$	$t_{2g}^6 e_g^4$

(B) Splitting of d orbitals in tetrahedral complexes

In a tetrahedral complex, the four ligands occupy alternate corners of a cube and the metal cation is placed in the centre. Here none of the d orbitals point directly towards the ligands; however, calculations reveal that the non-axial orbitals (d_{xy} , d_{yz} , d_{zx}) are closer to the ligands than the axial orbitals (d_{z^2} and $d_{x^2-y^2}$). Therefore the energy of t_{2g} orbitals is raised and e_g orbitals is lowered from the barycenter (barycenter is the weighted mean of these two sets of perturbed orbitals and is taken as zero). This is exactly opposite to what happens in an octahedral complex. The crystal field splitting is denoted by Δ_t where t stands for tetrahedral.

**Figure 20.8** Splitting of d orbitals in a tetrahedral crystal field

It has been observed that the energy separation between e_g and t_{2g} orbitals in tetrahedral complexes is smaller than in octahedral complexes because the d orbitals are not directly under the influence of the ligand and the number of ligands is smaller (4 in tetrahedral complex against 6 in octahedral complex).

The tetrahedral crystal field splitting (Δ_t) is nearly 4/9 that of octahedral crystal field splitting (Δ_o)

$$\Delta_t = 4/9 \Delta_o.$$

Since the value of Δ_t is small hence low spin (strong field) tetrahedral complexes have not been reported and only *high spin* or *spin free complexes* are formed.

(C) Crystal field splitting in square planar complexes:

The splitting of d orbitals in a square planar complex can be understood by gradually withdrawing two ligands lying along the z axis from an octahedral complex.

As the ligands lying on z axis are moved away, the electrons in the d orbitals along the z axis as well as in the xz and yz planes experience relatively smaller repulsions from the electrons of the ligands. This results in appreciable fall in the energy of d_{xy} , d_{yz} and d_{z^2} orbitals. These changes are shown in Figure 20.9. The crystal field stabilisation energy of square planar complex is indicated by Δ_{sp} and calculations reveal that $\Delta_{sp} = 1.3\Delta_o$.

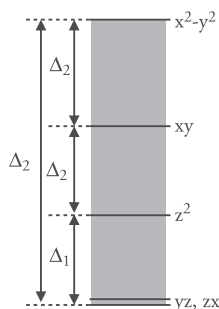


Figure 20.9 The orbital splitting parameters for a square-planar complex

Factors affecting magnitude of crystal field splitting:-

The magnitude of crystal field splitting Δ is influenced by several factors, some of which are discussed as follows:

- (i) *Geometry of the complex:* As discussed earlier the crystal field splitting for octahedral complex is nearly double that for tetrahedral complex

$$\Delta_t = 4/9 \Delta_o$$

This is attributed to the fact that

- The number of ligands in tetrahedral complex is 4 and that in octahedral complex is 6.
- In octahedral complex, the ligands approach along the axis influencing the axial d orbitals directly, whereas in tetrahedral complexes the d orbitals are not directly under the influence of the ligand.

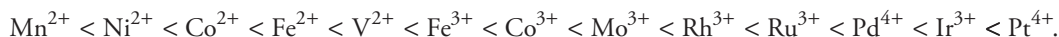
- (ii) *Nature of the ligands*: Some ligands produce more splitting than others. The crystal field splitting energy Δ_0 for $[\text{CrCl}_6]^{3-}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ is 163, 213, 259, 314 J/mol, respectively. In all the above complexes the cation is Cr^{3+} but the variation in ligand changes the value of Δ_0 .

Ligands like CN^- with higher value of Δ_0 are called strong field ligands and ligands like Cl^- with lesser value of Δ_0 are termed as weak field ligands. The ligands have been arranged in the order of their strength in spectrochemical series which has been discussed earlier (Section 20.8)

- (iii) *Charge on the metal ion*: According to crystal field theory the interaction between the metal ion and ligand is purely electrostatic in nature. Metal with higher charge produces more splitting than an ion with lower charge. For example Δ_0 for hexaqua complexes of Cr^{2+} and Cr^{3+} are 165.9 kJ/mol and 213 kJ/mol, respectively.
- (iv) *Position of the metal in the transition series*: It has been observed that the value of Δ_0 increases on descending down the group because down the group the size increases. Size of 4d and 5d orbitals are larger than 3d orbital hence the former have greater interaction with the ligands. In the same group, the crystal field splitting follows the order

$$5d > 4d > 3d.$$

For example, the value of Δ for $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Rh}(\text{NH}_3)_6]^{3+}$ and $[\text{Ir}(\text{NH}_3)_6]^{3+}$ is 296, 406 and 490 kJ/mol, respectively. In the above example all elements belong to the same group but Co^{3+} is in the 3d transition series, Rh is in 4d series and Ir is in the 5d transition series. The order of field strength for central metal ion is approximately



Applications of crystal field theory:

1. *Colour of transition metal complexes*: A sample appears coloured when it absorbs light in the visible region of the electromagnetic spectrum. Most of the transition metal complexes are coloured. The colour in these complexes is attributed to d-d transitions between t_{2g} and e_g orbitals. The energy difference between these two orbitals is so small that absorption of even small amount of light brings about the excitation from lower to a higher d level. However, it may be noted here that the d-d transitions are forbidden by the Laporte selection rule. The Laporte selection rule states that a transition can occur if Δl is ± 1 and therefore d \rightarrow d transitions are forbidden as $\Delta l = 0$.

Forbidden transitions do occur under certain circumstances but they usually have low intensities. Hence some other factors contribute to the colours of transition metal complexes. Franck Condon principle helps to explain these differences as several vibrational states exist within an electronic ground state. In accordance with Franck–Condon principle (for details refer section 17.3) the transition occurs from the lowest vibrational level in the electronic ground state and a higher vibrational level in the electronic excited state. The intensity of electronic transition is primarily due to changes in the vibrational energy. Both vibrational and electronic changes occur during the transitions, hence these transitions are termed as *vibronic transitions*. These bring about temporary change in the symmetry of the complex by removing its centre of symmetry. Thus the Laporte selection rule no longer applies and d \rightarrow d transitions are no longer forbidden.

The colour of the complex is complementary to the colour absorbed. For example, the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ where Ti^{3+} has one d electron in the t_{2g} orbital, on absorption of radiation this d electron is promoted to e_g orbital ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). It absorbs green and yellow light and transmits the complementary colour red and blue, hence it appears violet in colour. Similarly the complex $[\text{Co}(\text{NH}_3)_6]^{2+}$ appears red in colour as it absorbs the blue-green portion of visible light. It may be noted here that in absence of ligand, the compound appears colourless as there is no crystal field splitting. For example, on removal of water from $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$ on heating makes it colourless. Similarly $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue but anhydrous copper sulphate is white (Table 20.6 gives the colours of complex ions of d block elements).

Table 20.6 Colour of some complex ions of d block metals

Complex ion	Observed colour in aqueous solution
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Violet
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Violet
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	Blue
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Pale green
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Blue
$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$	Colourless
$[\text{Co}(\text{ox})_3]^{3-}$	Dark green
$[\text{Co}(\text{NH}_3)_6]^{3+}$	Orange
$[\text{Cu}(\text{en})_3]^{2+}$	Blue
$[\text{Co}(\text{CN})_6]^{3-}$	Yellow
$[\text{CoCl}_4]^{2-}$	Blue

- 2. Magnetic properties of complexes:** Whether a complex is high spin or low spin can be ascertained experimentally with the help of the magnetic properties of complexes. A complex having no unpaired electron is weakly repelled by the magnetic field and is said to be *diamagnetic*. The unpaired electrons of a complex having unpaired electrons will interact with the magnetic field generated by the spinning electrons and will be attracted by the magnetic field. Such a complex is termed as *paramagnetic* and the extent of attraction depends upon the number of unpaired electrons. Magnetic dipole moment represents the magnitude of paramagnetism and higher the value of magnetic dipole moment greater is the paramagnetism. There are two effects contributing to the magnetic dipole moment of a free atom or ion: the electron spin and the orbital angular momentum. However, when the atom or ion forms complex the orbital angular momentum is quenched and it becomes negligible, therefore the value of magnetic dipole moment is estimated by the *spin only* parameter.

The spin only magnetic moment is given by the formula

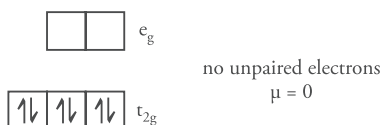
$$\mu_s = \sqrt{n(n+2)} \text{ B. M}$$

where n is the number of unpaired electrons and μ_s is the spin only magnetic moment in Bohr magneton.

The values of magnetic moments calculated from the spin only formula and those determined experimentally μ_{exp} are given in Table 20.7. The calculated and experimental values are in fair agreement with each other. For example $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$ is paramagnetic with μ_{exp} value 5.9, which is consistent with the calculated values showing that it has five unpaired electrons and its ground state electronic configuration will be high spin $t_{2g}^3 e_g^2$. Similarly magnetic

moment of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ are 0 and 4.9, respectively, showing the absence of unpaired electrons in $[\text{Co}(\text{NH}_3)_6]^{3+}$ and the presence of four unpaired electrons in $[\text{CoF}_6]^{3-}$ making the former a diamagnetic complex and the latter a paramagnetic complex (Fig 20.10). Similarly high spin Cu^{2+} (d^4) has four unpaired electrons and the value of μ calculated from spin only formula is $\sqrt{n(n+2)} = \sqrt{4 \times 6} = \sqrt{24} = 4.9$ whereas a low spin configuration has only two unpaired electrons and the observed value of magnetic moment is close to the expected value of 2.83.

(a) Low spin (diamagnetic) complex of $[\text{Co}(\text{NH}_3)_6]^{3+}$



(b) High spin (paramagnetic) complex of $[\text{CoF}_6]^{3-}$

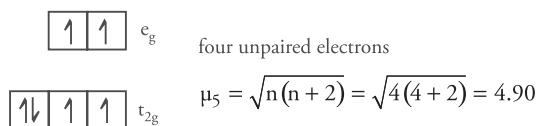


Figure 20.10 Diamagnetic and paramagnetic complexes of cobalt

Table 20.7 Values of μ_s and μ_{exp} in BM for high spin complexes of the elements of first row of transition series

Number of electrons in d orbital	Ions	Electronic configuration	μ_s	μ_{exp}
d^1	Ti^{3+}	t_{2g}^1	1.73	1.73-1.85
d^2	V^{3+}	t_{2g}^2	2.83	2.7-2.9
d^3	Cr^{3+}	t_{2g}^3	3.87	3.80

d ⁴	Mn ³⁺	$t_{2g}^3 e_g^1$	4.90	4.8-4.9
d ⁵	Fe ³⁺	$t_{2g}^3 e_g^2$	5.92	5.9
d ⁶	Fe ²⁺	$t_{2g}^4 e_g^2$	4.90	5.10-5.70
d ⁷	Co ²⁺	$t_{2g}^5 e_g^2$	3.87	4.3-5.2
d ⁸	Ni ²⁺	$t_{2g}^6 e_g^2$	2.83	2.8-4.0
d ⁹	Cu ²⁺	$t_{2g}^6 e_g^3$	1.73	1.7-2.2

From Table 20.7, it is clear that for high spin complexes the μ_s values agree with the μ_{exp} values.


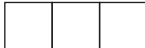
Limitations of crystal field theory

1. CFT lays emphasis only on the metal orbitals and ignores the ligand orbitals. In the metal orbitals also it considers only the metal d orbitals. It does not take into account other orbitals like the s, p_x, p_y and p_z orbitals. Neither does it consider the π orbitals of the ligand. Hence all properties of complexes dependent on the π -ligand orbitals cannot be explained by CFT; CFT does not consider π -bonding in complexes.
2. CFT is unable to explain the relative strengths of ligands. For example CFT offers no explanation as to why H₂O is a stronger ligand than OH⁻.
3. CFT considers the interaction between metal and ligand as purely ionic. It does not take into account the covalent character of metal ligand bonds.
4. CFT is unable to explain the π -bonding in complexes despite its frequent occurrence.

20.9 Molecular Orbital Theory

The crystal field theory treated metal and ligands as point charges and considers the interaction between them as purely electrostatic. Although the theory successfully explains the shape of complexes, their spectra and magnetic properties nevertheless it does not consider orbital overlap and completely ignores the covalent bonding in complexes. Molecular orbital theory considers the overlap of orbitals of central metal ion and ligands. It follows the basic postulates of MOT as discussed earlier (Section 10.12) and states that atomic orbitals of similar symmetry and energy overlap to form equal number of molecular orbitals (linear combination of atomic orbitals).

The application of molecular orbital theory to coordination compounds follows the basic terminology of group theory. Detailed discussion of group theory and its symbols is not possible here; however, we shall discuss in brief the terms to be used in the further description. The symbols for different orbitals are as follows:

s	singly degenerate		a _{1g} symmetry
p	triply degenerate		t _{1u} symmetry

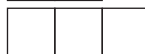
d has two types of orbitals

(i) doubly degenerate



e_g symmetry

(ii) triply degenerate



t_{2g} symmetry

The terms g and u stand for gerade and ungerade. Gerade implies that orbital has a centre of symmetry and does not change sign on inversion through the centre of molecule whereas ungerade implies that the centre of symmetry changes on inverting the molecule.

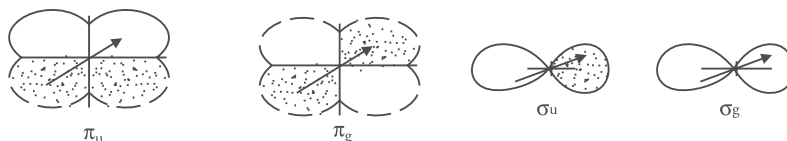


Figure 20.11 Gerade and ungerade orbitals

Sigma bonding in octahedral complexes

Consider a metal atom surrounded octahedrally by six ligands having filled p_σ and capable of forming σ bond with the metal ion represented as M. The metal and ligand orbitals with similar energies and symmetries overlap to form equal number of bonding and antibonding molecular orbitals. The s orbital of metal has a_{1g} symmetry, the three p orbitals have t_{1u} symmetry and the two d_{z^2} and $d_{x^2-y^2}$ have e_g symmetry. The ligand orbitals have symmetries $a_{1g} + t_{1u} + e_g$ which overlap with the s (a_{1g} symmetry), p (t_{1u} symmetry), d_{z^2} and $d_{x^2-y^2}$ (e_g symmetry) orbitals of metal ions to form bonding and antibonding orbitals. No combination of ligand σ orbitals has symmetry of the metal t_{2g} orbitals, hence the t_{2g} orbital remains a non-bonding orbital and does not participate in bonding. The t_{2g} orbitals are pure metal d orbitals whereas the e_g^* antibonding orbitals have major contribution from e_g orbitals of metal ion and minor contribution from the ligand orbitals.

The six ligands orbitals contribute $6 \times 2 = 12$ electrons which occupy the bonding a_{1g} , t_{1u} and e_g orbitals because the bonding molecular orbitals lie closer in energy to the ligand orbitals and are more like the ligand orbitals than the metal orbitals. The electrons present in the 3d orbitals of the metal are distributed between the t_{2g} orbitals and e_g^* orbitals because they have energies closer to the valence orbitals of the metal. The difference between the t_{2g} and antibonding e_g orbital is equal to the crystal field splitting parameter Δ_o of the crystal field theory. The filling of orbitals now depends upon the relative values of Δ_o and pairing energy P (discussed earlier). For example, if the metal has d^4 configuration first three electrons enter t_{2g} orbital and one may either pair in the t_{2g} orbital or may enter the e_g^* orbital depending upon the relative values of Δ_o and pairing energy P.

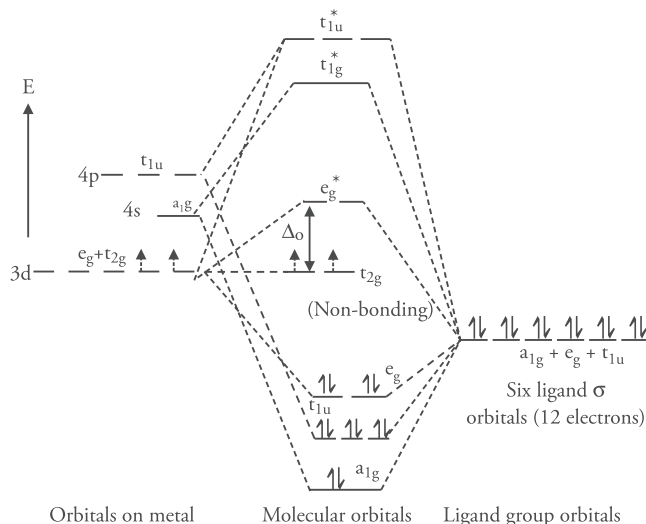


Figure 20.12 The molecular orbital energy level diagram for an octahedral complex

π – bonding in octahedral complexes

As studied earlier, the t_{2g} orbital of the metal remains a non-bonding orbital in the M – L σ bonded complexes as the σ orbitals of the ligand do not have a symmetry of the metal t_{2g} orbitals. However, ligands with π orbitals have atomic orbitals of t_{2g} symmetry which can overlap with the metal t_{2g} orbitals to form bonding and antibonding orbitals. Hence in π - bonding ligands the metal t_{2g} orbitals are no longer non-bonding but overlap with the ligand t_{2g} orbitals to form bonding and antibonding molecular orbitals. As a result relative energies of molecular t_{2g} orbitals may be above or below the energies of atomic t_{2g} orbitals, thereby increasing or decreasing the value of Δ_o .

Complexes with π donor ligands: A π donor ligand (such as F^- , Cl^- , Br^- , OH^-) has filled orbitals of π symmetry around the M–L axis so that electron density is donated to the metal empty t_{2g} orbitals. Hence $L \rightarrow M$ π donation occurs and the ligand acts as a lewis base (electron pair donor). The energy of the ligand π orbitals is lower than the metal d orbitals, hence when the π orbitals of the π donor ligands overlap with partially filled d orbitals of the metal, the t_{2g} bonding molecular orbital lies lower than the ligand orbitals and t_{2g} antibonding molecular orbital lies above the energy of the d orbitals of free metal atom. The π electrons of the ligand occupy the t_{2g} bonding molecular orbital (represented by solid arrow in Fig. 20.13) and the electrons of the d orbital of the metal atom (represented by dotted arrows in Fig. 20.13) occupy the t_{2g} antibonding molecular orbital. The net effect is that the t_{2g} orbital which was non-bonding molecular orbital in σ bonded ML complex becomes antibonding in complexes of metals with π donor ligands. Their energy level lies close to the antibonding e_g orbital resulting in decrease in the value of Δ_o .

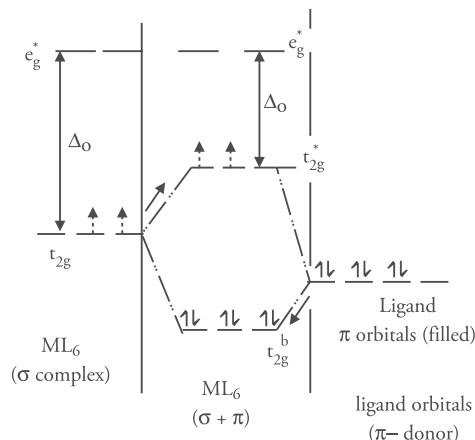


Figure 20.13 π -donor ligands decrease the value of Δ_o (only the ligand π -orbitals are shown)

Complexes with π acceptor ligands: These ligands (such as CO, CN^- , PR_3 , SR_2 , etc.) that can accept electrons from the metal d orbitals forming $M \rightarrow L$ bond. These ligands act as electron acceptors (Lewis acids). Unlike π donor ligands the energy of the ligand orbitals in π acceptor ligands is higher than the metal d orbitals. The ligand t_{2g} orbital overlaps with metal t_{2g} orbital (having largely metal d orbital character) from t_{2g} bonding molecular orbital that lies lower in energy than the d orbitals themselves. This increases the magnitude of Δ_o and this is the reason why CO, CN^- are called strong field ligands as they require high energy for transition.

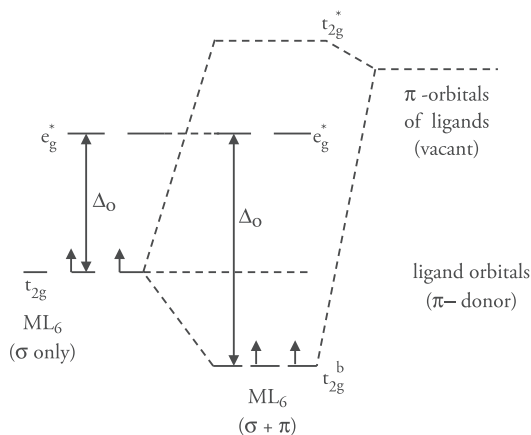
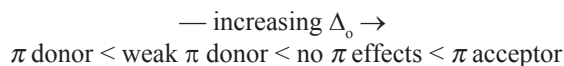


Figure 20.14 π -acceptor ligands increase the value of Δ_o (only the ligand π orbitals are shown)

The position of ligands in spectrochemical series can be interpreted on the basis of ML σ and π bonding. Value of Δ_o decreases for π donor ligands and increases for π acceptor ligands. The value of Δ_o follows the order



Examples of π donor ligands are F^- , Cl^- , Br^- , I^- ; H_2O is a weak π donor ligand; NH_3 has no π effects and PR_3 , CO are π acceptor ligands.

Molecular orbital diagram for tetrahedral complexes

A tetrahedral complex may be thought to be derived from a cube with p_σ orbital of the ligand directed towards the metal ion. The s orbital of the metal has a_1 symmetry, whereas the three p orbitals and three d orbitals (d_{xy} , d_{xz} , d_{yz}) orbitals) have t_2 symmetry. The ligand p_σ orbitals have a_1 and t_2 symmetry. Hence these orbitals overlap effectively to form the bonding and antibonding orbitals. The d_{z^2} and $d_{x^2-y^2}$ orbitals of metal have e symmetry and do not take part in bonding as

there are no combinations of p_σ orbitals of the ligands with e symmetry. A simple molecular orbital energy level diagram of a tetrahedral complex is shown in Figure 20.15. The t_2 orbitals of the ligand overlap with the t_2 orbitals of the metal ion (i.e., the set of p orbitals and d_{xy} , d_{xz} , d_{yz} orbitals) to form t_2^b , t_2 and t_2^* . These molecular orbitals have a mixed contribution from the p and d orbitals of the metal ion.

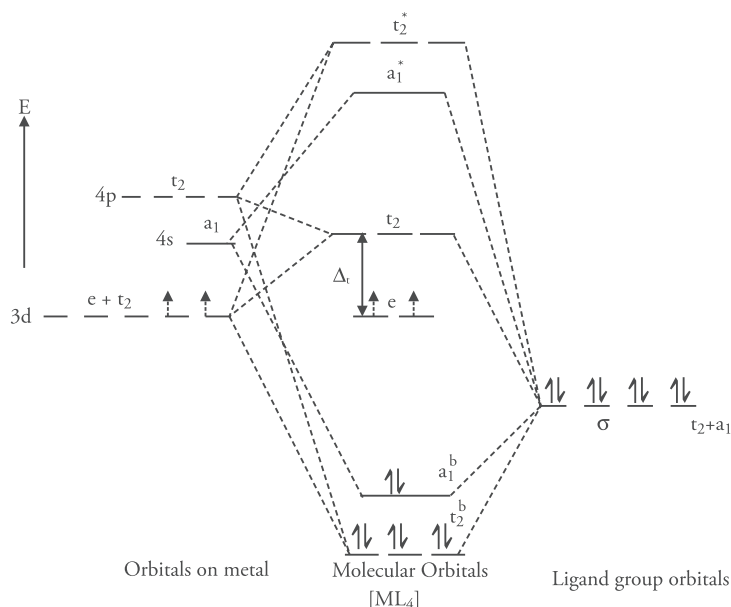


Figure 20.15 A qualitative molecular orbital diagram for a tetrahedral complex

The eight electrons contributed by the four ligands (shown by solid arrows) occupy the t_2^b and a_1^b orbitals. The electrons present in d orbital of free metal ion (shown by dotted arrows) are distributed in the e and t_2 orbitals. The e orbitals are the non-bonding metal ion d_{z^2} and $d_{x^2-y^2}$ orbitals, whereas the t_2 orbitals have major contribution from the d or p orbitals of the metal ions. The energy difference between e and t_2 is equivalent to the crystal field splitting parameter Δ_t (subscript t stands for tetrahedral). However, in crystal field theory the e and t_2 orbitals are pure

d orbitals but according to molecular orbital theory e orbitals are pure metal d orbitals but t_2 orbitals have mixed p, d orbital character. Hence the $e \rightarrow t_2$ transition in tetrahedral complex is less $d \rightarrow d$ type than $t_{2g} \rightarrow e_g$ transition in octahedral complex. So they are more allowed and occur at higher ϵ values.

Note that a tetrahedron does not have a centre of symmetry, hence the subscript g (gerade) and u (ungerade) are not used.

Summary

- Coordination compounds are complex salts consisting of either a complex cation and simple anion or simple cation and complex anion or even complex cation and complex anion.
- A ligand is an atom, ion or molecule capable of donating an electron pair to the central metal ion. Ligands can be monodentate with one donor atom or polydentate with more than one donor atom.
- Ligancy or coordination number is the total number of ligand atoms that coordinate with the central metal atom.
- Coordination compounds are named as per the guidelines laid down by IUPAC.
- Coordination compounds exhibit both structural and stereoisomerism.
- Structural isomers have same molecular formula but vary in structural arrangement of atoms. *Ionisation isomers* have same molecular formula but give different ions in solution. In *hydrate isomerism* the number of water molecules inside and outside the coordination sphere vary. *Coordination isomerism* is exhibited by complex having both complex cation and complex anion. In this, the ligands are exchanged between the cationic and anionic parts. *Linkage isomerism* is shown by ambidentate ligands having two different donor atoms. *Coordination position isomerism* occurs in polynuclear or bridged complexes due to exchange of ligands between different metal nuclei.
- Stereoisomerism arises due to difference in spatial arrangements of ligands around the central metal atom.
- *Geometrical isomers*: Disubstituted complexes with coordination numbers 4 and 6 exhibit geometrical isomerism. If similar ligands are adjacent to each other the isomer is a *cis* isomer and if they are opposite then it is a *trans* isomer.
- *Optical isomers*: Compounds that form non-superimposable mirror image and rotate the plane of polarised light.
- Bonding in coordination compounds is explained by Werner's theory, Sidgwick effective atomic number theory, valence bond theory crystal field theory and molecular orbital theory.
- Werner postulated that a coordination metal shows two types of valencies: Primary or ionizable valency which is non-directional and secondary or non-ionizable valency which is directional. The secondary valency corresponds to the coordination number of the metal ion and imparts a definite geometry and stereochemistry to the complex.

- Sidgwick explained the structure on the basis of Lewis concept. The ligands are electron pair donors and he postulated that a stable complex is formed when the total number of electrons on the central metal atoms (electrons on metal + electrons donated by the ligands) is equal to the atomic number of the next noble gas. This was termed as the *effective atomic number*. However, not all complexes were found to follow this rule.
- Valence bond theory (VBT) is based on the concept of hybridisation and states that the central metal atom makes available s, p, d orbitals to accommodate the electron pairs donated by the ligand.
- Crystal field theory considers the ligands as point charges and the interaction between metal orbitals and ligands as purely electrostatic. The approaching ligands split the degenerate d orbitals into two sets of different energies (t_{2g} and e_g orbitals). This splitting is termed as crystal field splitting (Δ). The electron donated by ligands are accommodated in these orbitals.
- Ligands can be weak field or strong field. For weak field ligands the crystal field splitting (Δ) is less and the complexes formed will be *high spin* or *spin free*.
- If the ligands are strong, value of Δ is high and the complexes are *spin paired* or *low spin*.
- Crystal field splitting is influenced by the nature of ligands, geometry of the complex, charge on metal ion and position of metal in the transition series.
- Crystal field theory (CFT) explained colour of complexes on the basis of d-d transitions and could also explain the magnetic properties of complexes.
- Molecular orbital theory considers both the metal and ligand orbitals, it also considers covalent and π bonding in complexes.
- Molecular orbital theory was able to explain why some ligands are strong field and others are weak field ligands.

Review Questions

1. What is coordination chemistry? With reference to coordination chemistry explain the terms ligand, coordination number, coordination sphere and complex ion.
2. Do coordination compounds show isomerism? Illustrate the following with the help of suitable examples
 - (i) Ionisation isomerism
 - (ii) Hydrate isomerism
 - (iii) Coordination isomerism
 - (iv) Linkage isomerism
 - (v) Coordination position isomerism
3. With the help of suitable examples, explain stereoisomerism in coordination compounds.
4. Who made the first attempt to explain bonding in coordination compounds? With the help of a suitable example, explain the basic postulates of his theory.

5. State and explain Sidgwick's coordination theory. Calculate the EAN of the following complexes:
 - (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - (ii) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+}$
 - (iii) $[\text{Ni}(\text{en})_3]^{2+}$
 - (iv) $[\text{CuCl}_2]^-$
 - (v) $[\text{Cd}(\text{NH}_3)_4]^{2+}$
6. With the help of valence bond theory explain bonding in the following complexes:
 - (i) $[\text{NiCl}_4]^{2-}$
 - (ii) $[\text{Ni}(\text{CO})_4]$
 - (iii) $[\text{Ni}(\text{CN})_4]^{2-}$
 - (iv) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - (v) $[\text{CoF}_6]^{3-}$
7. With the help of suitable example, explain the formation of inner orbital and outer orbital complexes in coordination compounds. Why are inner orbital and outer orbital complexes called spin paired or low spin and spin free or high spin complexes, respectively?
8. Who propounded the crystal field theory to explain bonding in coordination compounds? Write down the basic postulates of this theory.
9. What do you understand by crystal field stabilisation energy (CFSE) and pairing energy (P)? Describe and compare the splitting of d orbitals under the influence of octahedral and tetrahedral ligand fields.
10. How does crystal field theory explain the colour of various transition metal complexes?
11. Explain the distribution of electrons in the presence of strong field and weak field ligands for a central atom having d^4 , d^5 , d^6 and d^7 electrons, respectively. Also explain various factors affecting the magnitude of crystal field splitting.
12. Explain how the crystal field theory helps in predicting the magnetic properties of transition metals.
13. Write IUPAC name of the following compounds:
 - (i) $[\text{CoCl}(\text{NH}_3)_4(\text{NO}_2)]\text{Cl}$
 - (ii) $[\text{PtCl}(\text{NH}_2\text{Me})(\text{NH}_3)_4]\text{Cl}$
 - (iii) $\text{K}_2[\text{PdCl}_4]$
 - (iv) $[\text{Fe}(\text{CNMe})_6]\text{Br}_2$
 - (v) $[\text{Co}(\text{en})_3]\text{Cl}_3$
14. How does molecular orbital theory explain bonding in sigma bonded octahedral complexes?
15. Draw the energy level diagram for the sigma bonded tetrahedral complex.
16. How can the position of a ligand in spectrochemical series be interpreted with the help of molecular orbital theory?
17. With the help of molecular orbital theory explain the π bonding in octahedral complexes.

Multiple Choice Questions

- Which of the following is a polydentate ligand
 - Ammonia
 - Carbonyl
 - Nitrosyl
 - Ethylenediaminetetraacetic acid
- Solution of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ produces
 - Six ions
 - Four ions
 - Three ions
 - Two ions
- The oxidation state of central metal ion in $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$ is
 - +4
 - +3
 - +1
 - +2
- $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]\text{SCN}$ and $[\text{Co}(\text{en})_2\text{NO}_2\text{SCN}]\text{Cl}$ are examples of
 - Linkage isomers
 - Ionisation isomers
 - Coordination isomers
 - Optical isomers
- The IUPAC name of $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$ is
 - Potassium pentacyanonitrosylferrate(III)
 - Potassium pentacyanidonitrosylferrate(II)
 - Tripotassiumpentacyanidonitrosylferrite (II)
 - Tripotassiumpentacyanonitrosylferrate (III)
- The crystal field splitting energy for octahedral (Δ_o) and tetrahedral complexes (Δ_t) are related as
 - $\Delta_o = 2\Delta_t$
 - $\Delta_t = \frac{1}{2}\Delta_o$
 - $\Delta_t = \frac{4}{9}\Delta_o$
 - $\Delta_o = \frac{4}{9}\Delta_t$
- Each of the following compounds $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3$, $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$ and $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is dissolved in water to make a 0.01M solution. The order of increasing conductivity in solution is
 - $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5] < [\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2 < [\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3 < \text{K}_4[\text{Fe}(\text{CN})_6]$
 - $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3 < \text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5] < [\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2 < \text{K}_4[\text{Fe}(\text{CN})_6]$
 - $\text{K}_4[\text{Fe}(\text{CN})_6] < [\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3 < \text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5] < [\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$
 - $\text{K}_4[\text{Fe}(\text{CN})_6] < [\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Br}_3 < [\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2 < \text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$
- The number of unpaired electrons in d^6 , low spin octahedral complex is
 - 4
 - 3
 - 1
 - 0
- Among $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$
 - $[\text{Ni}(\text{CO})_4]$ and $[\text{NiCl}_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic.
 - $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CO})_4]$ is paramagnetic.

- (c) $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{NiCl}_4]^{2-}$ is paramagnetic.
 (d) $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic and $[\text{Ni}(\text{CO})_4]$ is diamagnetic.
10. Which of the following complexes has the lowest Δ_o value
 (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (b) $[\text{CoF}_6]^{3-}$
 (c) $[\text{Ir}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Rh}(\text{NH}_3)_6]^{3+}$
11. Which of the following complexes has maximum Δ_o value
 (a) $[\text{Cr}(\text{CN})_6]^{3-}$ (b) $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (d) $[\text{CrCl}_6]^{3-}$
12. Which of the following set of ions will be colourless
 (a) Zn^{2+} , Cu^{2+} , Ti^{3+} , Co^{2+} (b) Zn^{2+} , Cu^+ , Ti^{4+} , V^{2+}
 (c) Cr^{3+} , Mn^{2+} , Zn^{2+} , Ti^{4+} (d) Mn^{7+} , Cr^{6+} , Cu^+ , V^{2+}
13. Which of the following complexes will not show optical isomerism
 (a) $[\text{Cr}(\text{ox})_3]^{3-}$ (b) $\text{trans} [\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 (c) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ (d) $[\text{Co}(\text{EDTA})]^-$
14. In spectrochemical series, which of the following ligands has a strong field
 (a) NO_3^- (b) H_2O
 (c) Cl^- (d) CO
15. Which of the following complex obeys the Sidgwick EAN rule
 (a) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (b) $[\text{CuCl}_2]^-$
 (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
16. According to the group theory the p orbitals in octahedral complexes have the symmetry
 (a) a_{1g} (b) t_{1u}
 (c) e_g (d) t_{2g}
17. Which of the following is a non-bonding orbital in σ bonded octahedral and tetrahedral complexes respectively
 (a) t_{2g} and e respectively (b) e_g and t_2 respectively
 (c) t_{2g} and t respectively (d) e_g and e respectively.
18. π -donor ligands ----- the value of Δ_o , whereas π -acceptor ligands ----- the value of Δ_o
 (a) Decrease, decrease (b) Increase, increase
 (c) Decrease, increase (d) Increase, decrease

Solution

- | | | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 (d) | 2 (b) | 3 (a) | 4 (b) | 5 (b) | 6 (c) | 7 (a) | 8 (d) |
| 9 (c) | 10 (b) | 11 (a) | 12 (b) | 13 (b) | 14 (d) | 15 (c) | 16 (b) |
| 17 (a) | 18 (c) | | | | | | |

Chapter 21

ORGANOMETALLIC COMPOUNDS

21.1 Introduction

An organometallic compound is a compound which possesses metal–carbon bond $M^{\delta+} - C^{\delta-}$. Example $(C_2H_5)_2Zn$, $(CH_3)_4Si$, $(C_5H_5)_2Fe$ (ferrocene), $K[PtCl_3(C_2H_4)]$ (Ziese's salt), $Ni(CO)_4$ etc. It may include B, Si, Ge, As, Sb, Se and Te.

It is important to note that a compound like $B(OCH_3)_3$ is not an organometallic compound as it does not have a metal–carbon bond whereas $B(CH_3)_3$ having a metal–carbon bond is an organometallic compound.

However, inspite of definitions the borderline that distinguishes organometallic compounds from other compounds is unclear. For example, metal cyanides ($M-CN$) and metal carbides (CaC_2 , Al_4C_3 etc.), metal carbonates, contain metal–carbon bond but are not considered as organometallics because their properties are closely related to inorganic compounds. On the other hand $Ni(CO)_4$ is considered as an organometallic compound although carbonyl group is hardly a typical organic compound. The organometallic compounds are classified on the basis of the nature of metal–carbon bond.

(i) Ionic Organometallic Compounds

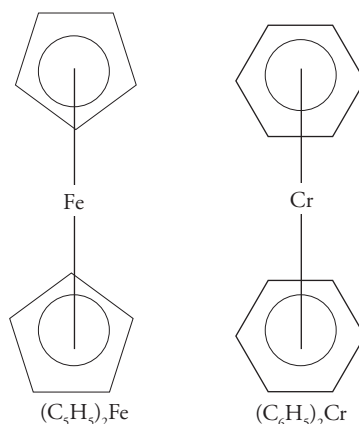
Organometallic compounds with highly electropositive metals are ionic in nature. Carbon of the organic group carries a negative charge which is strongly attracted by the positively charged metal ion by electrostatic forces of attraction. Examples include $C_6H_5Na^+$, $C_5H_5^-Na^+$, $C_5H_5^-K^+$, etc.

These compounds are very reactive, have high melting point and are almost insoluble in non-polar solvents.

(ii) Covalent Organometallic Compounds

In such compounds there exists a covalent bond between the metal atom and the organic group. They can be of various types

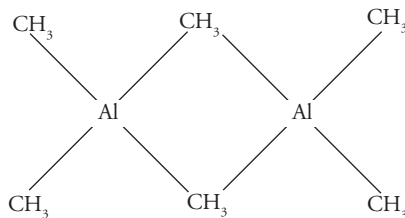
- (a) **Sigma bonded organometallic compounds** The metal is bonded to a carbon atom by a normal sigma covalent bond. The covalent organometallic compounds are generally metal alkyl compounds. Examples include $\text{Pb}(\text{C}_2\text{H}_5)_2$, $(\text{C}_6\text{H}_5)_2\text{Zn}$, $(\text{CH}_3)_2\text{Cd}$, $\text{C}_4\text{H}_9\text{Li}$, Grignards reagents, etc. The polarity of the bond depends upon the difference in electronegativity between metal and carbon atom.
- (b) **pi bonded organometallics** In this type of organometallic compounds there is an interaction between the π orbitals of organic ligands and the d and or p orbitals of the metal atoms (particularly transition metals). The metal forms a complex with alkenes as well as cyclic compounds having delocalised π orbitals as found in cyclopentadiene or benzene. Examples include ferrocene where iron is sandwiched between two parallel cyclopentadiene rings. These form a special class of compounds called 'sandwich compounds'.



Similar π -complex of alkene with metal ion was first reported by Zeise (a Danish chemist) and is known as Zeise salt $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$, carbonyls like $\text{Ni}(\text{CO})_4$ are also complexes of π acceptor ligands.

- (c) **Organometallic compounds having bridging alkyl groups**

Example: dimeric trialkylaluminium

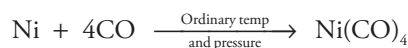
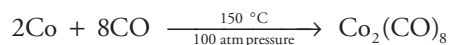
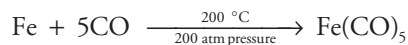


Dimeric trialkylaluminium

21.2 General Methods of Preparation

The various methods of preparation of organometallic compounds are as follows:

- (i) **Reaction of CO with metals** Metals like Ni, Fe and Co react with CO under controlled conditions to form carbonyls.



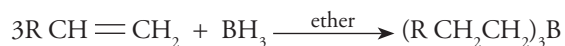
- (ii) **Reactions of metals with olefins**



- (iii) **Hydrometallation or addition of metal hydrides to unsaturated hydrocarbons**



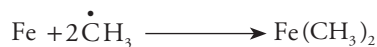
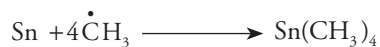
Example is hydroboration reactions



- (iv) **Methods involving free radicals** The general reaction is



The free radicals produced by the pyrolysis of tetramethyl lead were made to react with metals like Fe, Sn and Zn to form the corresponding methyl compounds.



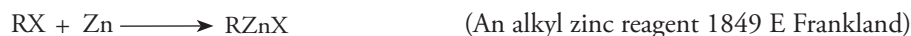
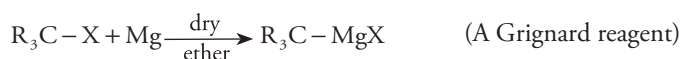
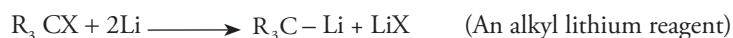
- (v) **Reaction of metals with hydrocarbons** Hydrocarbons having acidic hydrogen atoms react with highly electropositive metals to form organometallic compounds



Cyclopentadiene reacts with metals such as potassium and iron to form organometallic compounds



- (vi) **Direct synthesis**

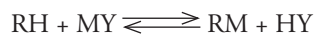


- (vii) **Transmetallation on Metal Exchange Reactions**

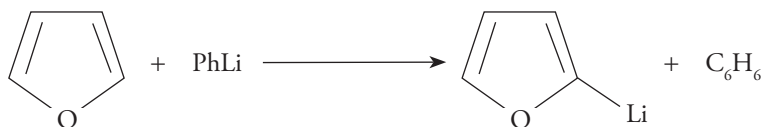
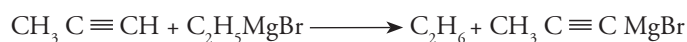
Many organometallic compounds are prepared by metal exchange reactions



- (viii) **Metallation reactions** Reactions where metal hydrogen exchange occurs are called metallation reactions. The general reaction is



Example

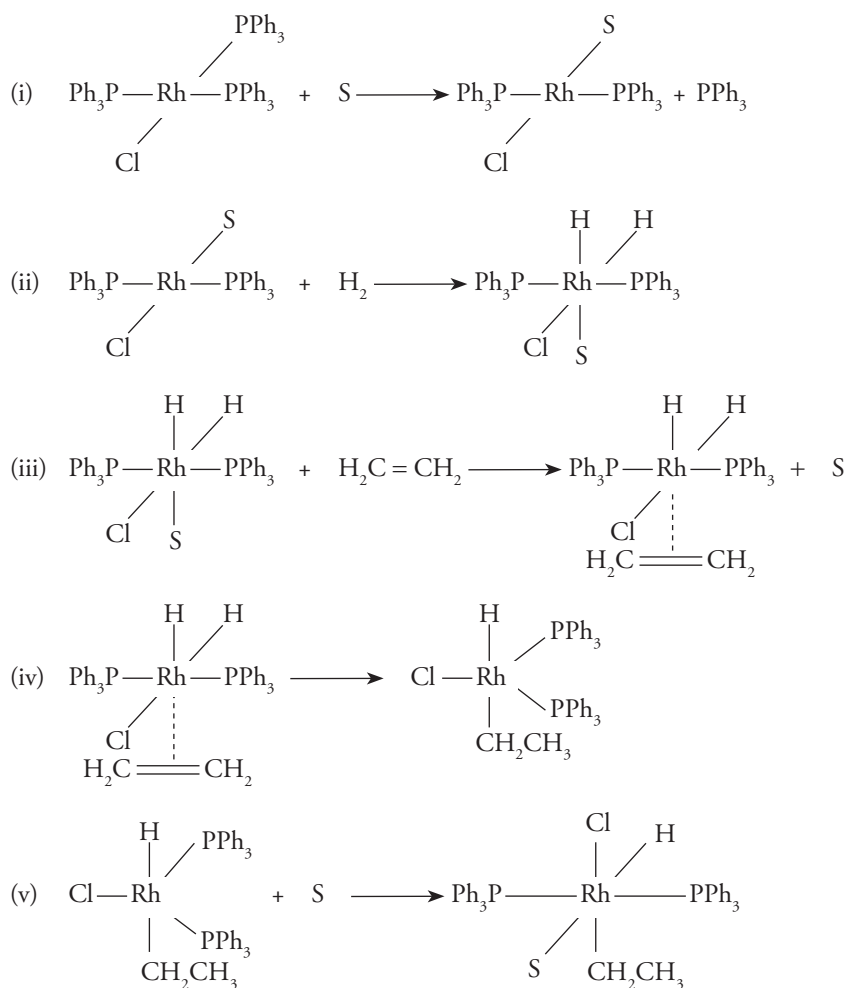


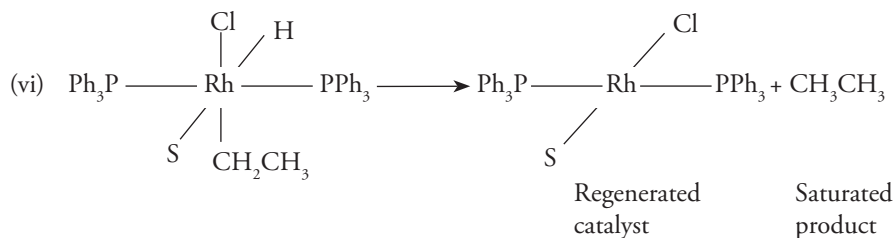
21.3 Applications of Organometallics

- Wilkinsons Catalysts (Hydrogenation of alkenes)** Wilkinsons catalyst, discovered by Sir Geoffrey Wilkinson is a complex of a transition metal rhodium. Having the formula $\text{RhCl}(\text{PPh}_3)_3$ where Ph stands for phenyl group, Wilkinsons catalyst, chlorotris (triphenylphosphine) rhodium I is widely used for the homogenous hydrogenation of alkenes.

The catalyst undergoes solvation followed by oxidative addition of a molecule of hydrogen. The alkene then coordinates and reacts with a hydrogen to form an alkyl group due to the migration of hydride ion from metal to a carbon atom. Reactions of this type are termed as '*insertion reactions*'.

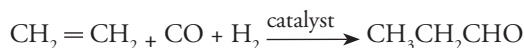
The overall reaction of hydrogenation with Wilkinsons catalyst appears to be as follows



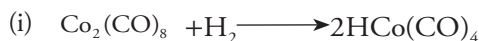


2. Oxo process or Hydroformylation

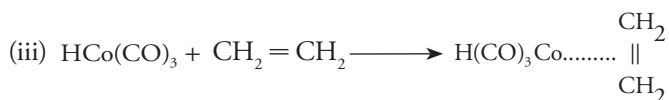
Organometallics are found to catalyse the conversion of alkenes into alcohols (which find use in detergent manufacturing). Octacarbonyl dicobalt $\text{Co}_2(\text{CO})_8$, catalyses the conversion of alkenes into aldehydes in the presence carbon monoxide and hydrogen. The aldehydes are further reduced to form alcohols.



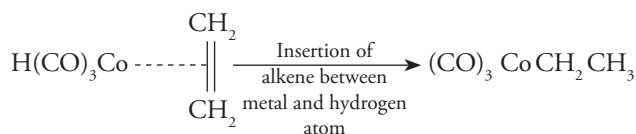
The reaction occurs in the following steps



Hydrido tetracarbonyl cobalt



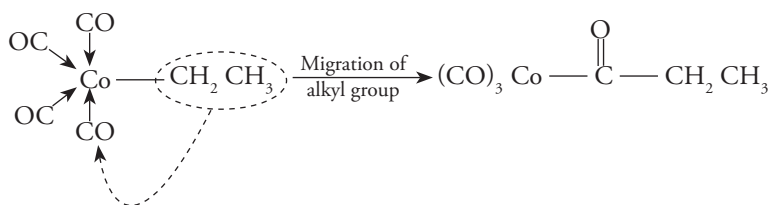
(iv) Hydrogen migrates from CO to one of the carbon atom of alkene and the other carbon atom of alkene attaches itself to cobalt forming metal alkyl.

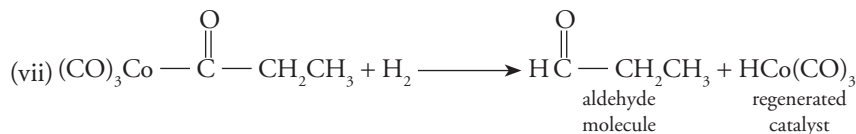


(v)



(vi) Migration of alkyl group to carbonyl group forming carbon-carbon bond





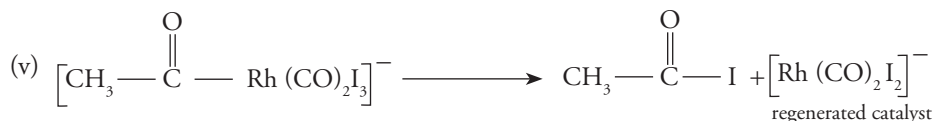
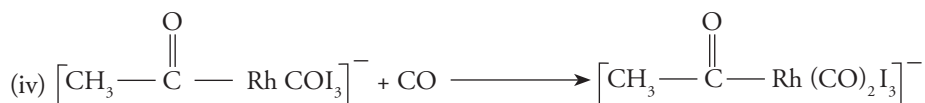
The above reactions are examples of '*carbonyl insertion*' as the carbon monoxide ligand from the cobalt is inserted between cobalt atom and the alkyl group.

3. Manufacture of acetic acid

Rhodium catalyst is used to insert carbon monoxide into methanol to produce acetic acid.



The process catalysed by rhodium carbonyl iodide involves oxidative addition, insertion and reductive elimination resulting in the production of acetic acid by insertion of carbon monoxide into methanol. The oxidation state of rhodium varies from +1 to +3. The reaction is believed to occur in the following steps.



HI formed is utilised in the step (i).

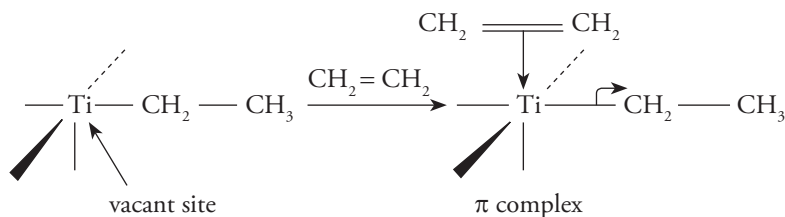
The above process is used world wide to produce acetic acid (Monsanto acetic acid process).

4. Polymerisation

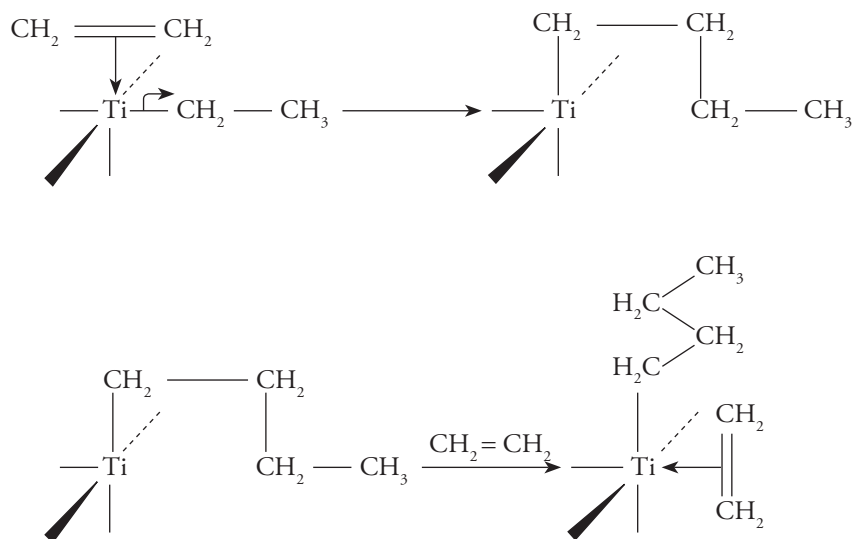
The reactions discussed so far are examples of homogenous catalysis. The reactants and the catalyst are soluble in the solvent used. The polymerisation of alkenes using Ziegler-Natta catalyst is an example heterogenous catalysis. This catalyst was discovered by Karl Ziegler and Giulio Natta who jointly received Nobel Prize in 1963 for developing this catalyst. This catalyst has revolutionised the field of polymer chemistry.

Ziegler–Natta catalyst comprises of a transition metal salt like titanium trichloride in combination with a metal alkyl like triethylaluminium. The two react to form a complex having an ethyl group in situ.

The alkene which has to undergo polymerisation forms a π bond with titanium forming a π complex.



The ethylene unit inserts itself between the titanium and the alkyl group.



The chain extends further. It is terminated by the insertion of hydrogen atom between titanium atom and the alkyl chain.

21.4 Grignard Reagents

Grignard reagents are the compounds of general formula $R-Mg-X$, where R is a hydrocarbon radical and X is a halogen atom. These reagents were first prepared by Victor Grignard in 1900 and it was found that they can be used to prepare almost all classes of organic compounds. Due to the immense utility of these compounds Grignard was awarded the Noble Prize in 1912.

Methyl magnesium iodide, CH_3MgI , is a typical representative of Grignard reagents.

Preparation of methyl magnesium iodide.

CH_3MgI is prepared by the action of very pure and dry methyl iodide on scrupulously clean and dry (alcohol-free) ether.

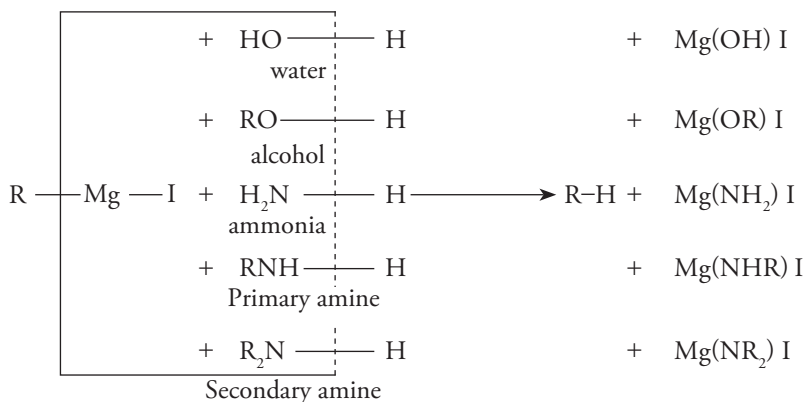
In the preparation of Grignard reagent, diethyl ether is usually employed as solvent. This ether must be alcohol-free because the latter reacts with the Grignard reagent formed. (See reactions of Grignard reagents with compounds containing active hydrogen). Acetone also cannot be used as a solvent as it also reacts with Grignard reagent.

A suspension of clean and dry magnesium ribbon (1 mole) cut into small pieces, in absolutely dry and pure (alcohol-free) ether is stirred mechanically. An ether solution of methyl iodide (1 mole) is gradually run in. A trace of iodine is usually added to initiate the reaction. Once the reaction starts it proceeds vigorously with the evolution of heat. Sometimes, the reaction is so violent that the reaction mixture has to be cooled in running water. The reaction mixture is then warmed under reflux on a steam bath for sometime to complete the reaction. An almost clear solution of CH_3MgI in ether is thus obtained which is used as such for synthetic purposes. The solvent, ether is not evaporated out as the solid Grignard compound tends to explode. The following precautions must be observed in the preparation of a Grignard compound.

- (i) The apparatus must be perfectly clean and dry.
- (ii) The calcium chloride guard tubes must be used to prevent the hydrolysis of Grignard reagent by atmospheric moisture.
- (iii) The reagents employed in the reaction must be absolutely pure and dry. Ether must be alcohol free.

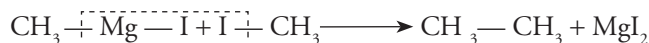
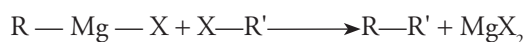
Applications of Grignards reagents**1. Synthesis of hydrocarbons****(a) Alkanes**

- (i) **With compounds containing active hydrogen atom.** Grignard reagents, R-MgX , react with compounds containing active hydrogen such as water, alcohols, ammonia, primary and secondary amines, 1-alkynes, phenols and so on to give the alkane, R-H .



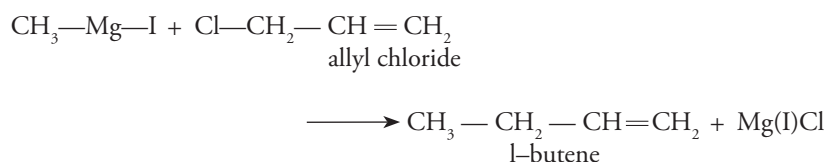
These reactions form the basis of the Zerewitinoff's method of determining active hydrogen atom in a molecule. This is done by measuring the volume of methane evolved.

- (ii) **With alkyl halides.** Higher alkanes are obtained when a Grignard reagent is treated with an alkyl halide.

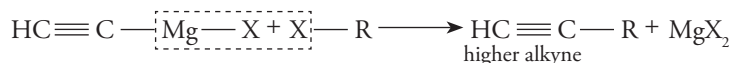
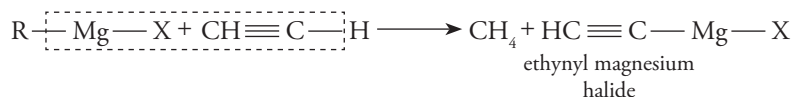


(b) **Alkenes**

With alkenyl halides. Grignard reagents react with alkenyl halides to give higher alkenes.



- (c) **Alkynes (higher)** 1-alkynes can be prepared by treating an alkyl magnesium halide with acetylene to get ethynyl magnesium halide (also a Grignard reagent) which on treatment with alkyl halide gives higher alkyne.

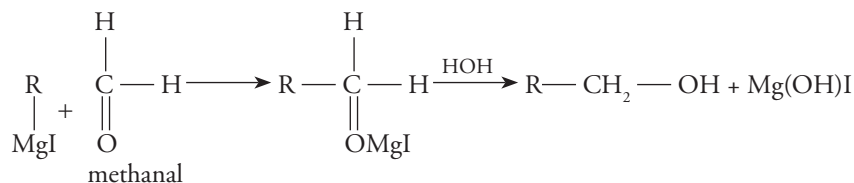


2. Synthesis of alcohols

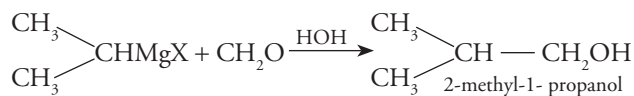
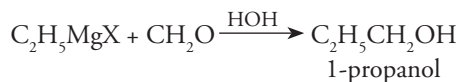
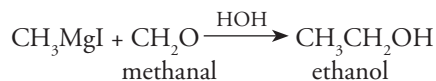
(a) Primary alcohols

(i) With methanal (formaldehyde)

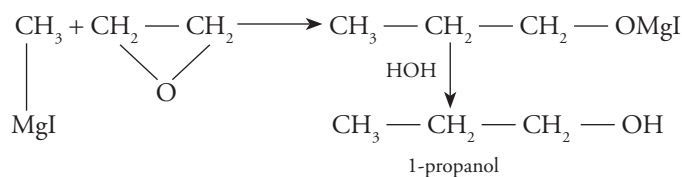
Formaldehyde reacts with a Grignard reagent to give an addition product which on hydrolysis yields a primary alcohol. In this method, there is an increase of one carbon atom in the chain.



Thus methyl magnesium iodide reacts with formaldehyde to give ethanol while n-propyl alcohol is obtained from C_2H_5MgI and $HCHO$.



- (ii) **With ethylene oxide** A primary alcohol can also be obtained by the reaction of a Grignard reagent and ethylene oxide.



It may be noted that in this reaction the resulting alcohol contains two carbon atoms more than the Grignard reagent.

Practice Problems

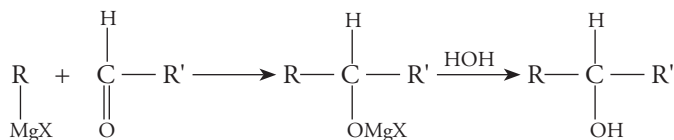
1. How will you obtain the following from suitable Grignard reagents

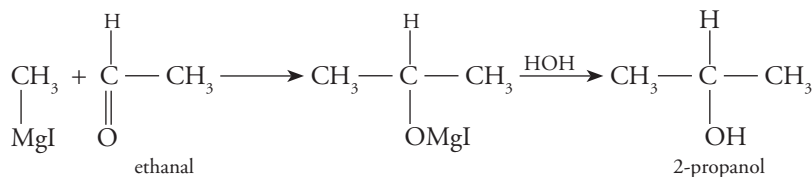
- (i) neopentyl alcohol (2, 2-dimethyl-1-propanol)
- (ii) isoamyl alcohol (3-methyl-1-butanol)
- (iii) 2, 3-dimethyl-1-butanol
- (iv) benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$)

(b). **Secondary alcohols**

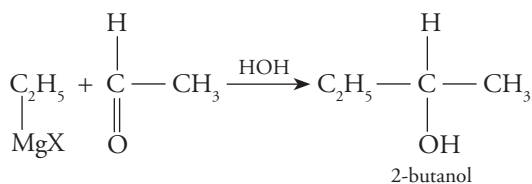
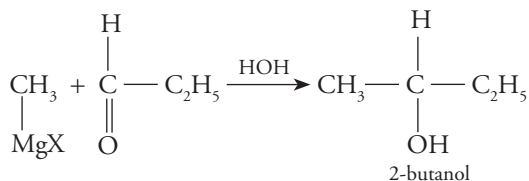
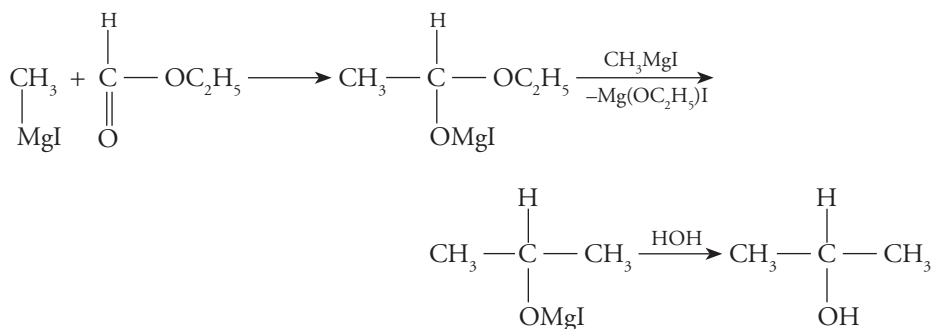
- (i) **With aldehydes other than formaldehyde**

Aldehydes other than formaldehyde react with $\text{R}-\text{Mg}-\text{X}$ to give the adducts which on hydrolysis give the secondary alcohols.





(i) **With one mole of formic ester and two moles of CH_3MgI**



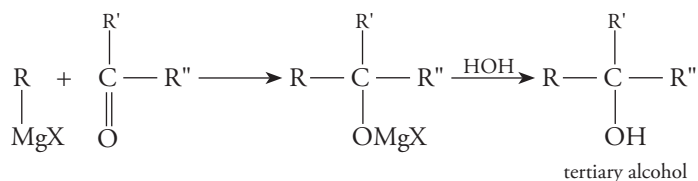
Practice Problems

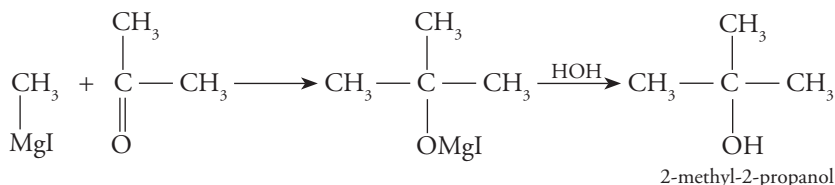
- Starting from a suitable Grignard reagent and acetaldehyde, how will you prepare
 - 2-propanol
 - 2-butanol
 - 2-pentanol
 - 3-pentanol

(c) Tertiary alcohols

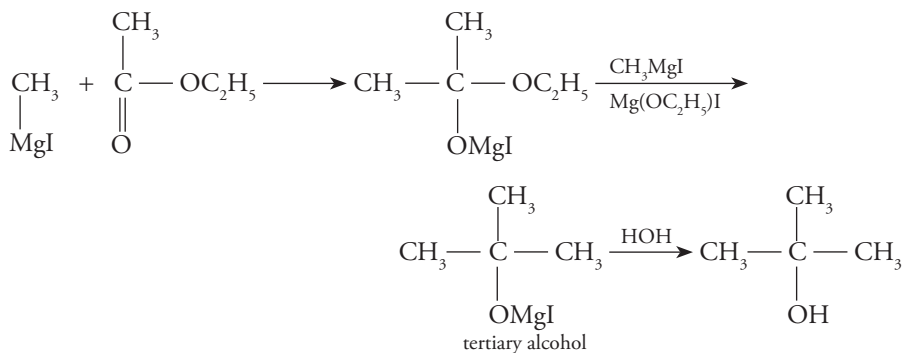
(i) With ketones

Ketones react with $\text{R} - \text{MgX}$ to form adducts which give tertiary alcohols on hydrolysis.





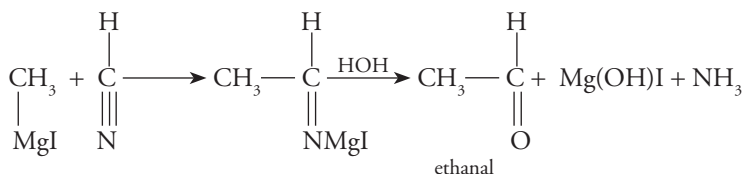
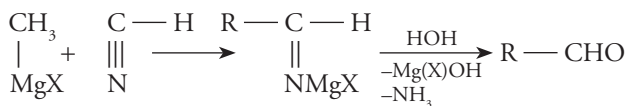
(ii) **With one mole of ester other than formic ester and two moles of CH_3MgI**



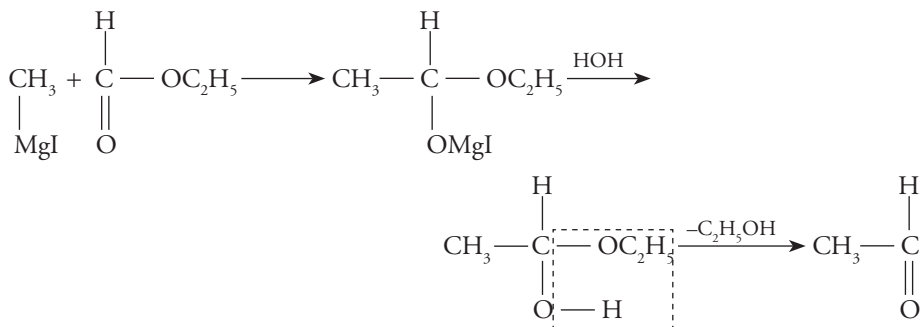
3. Synthesis of alkanals (aldehydes)

(i) **With hydrogen cyanide**

Grignard reagents react with HCN and the intermediate products are hydrolysed to aldehydes.

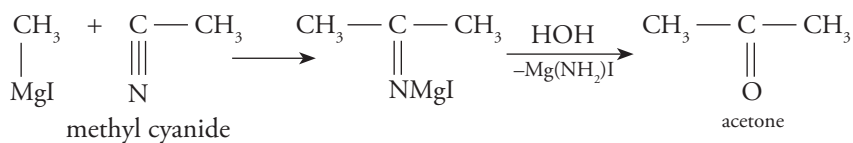
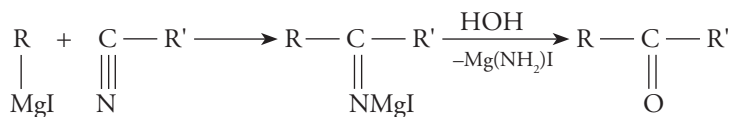


(ii) **With one of formic ester and one mole CH_3MgI**

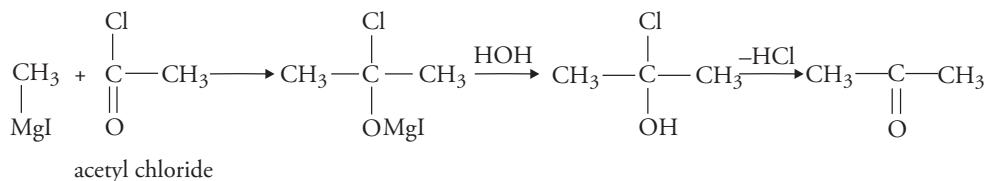
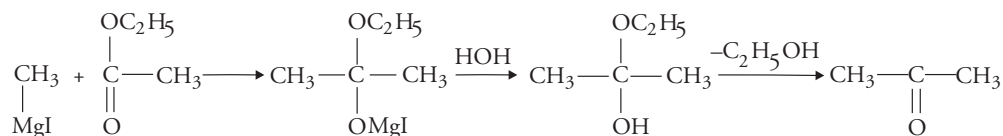
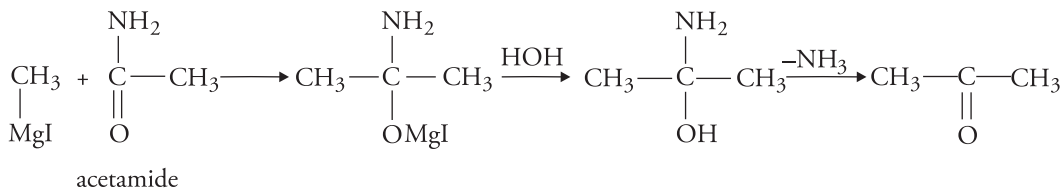


4. **Synthesis of alkanones (ketones)**(i) **With alkyl cyanides (cyanoalkanes or acid nitriles)**

Ketones are synthesised by the hydrolysis of the adduct obtained by the reaction of $R-MgI$ with $R-CN$.

(ii) **With acyl halides**

Ketones can also be prepared from acid halides as shown below

(iii) **With one mole of an ester other than formic ester and one mole of CH_3MgI .**(iv) **With acid amides**

Practice Problems

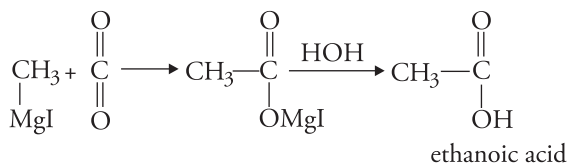
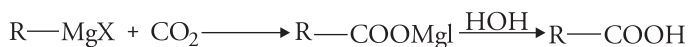
How will you obtain the following via a suitable Grignard reaction?

(i) 2-butanone

(ii) 3-pentanone

5. **Synthesis of alkanolic acids (carboxylic acids) with carbon dioxide**

Fatty acids are synthesised by the reaction of a Grignard reagent with carbon dioxide and then hydrolysing the adduct.



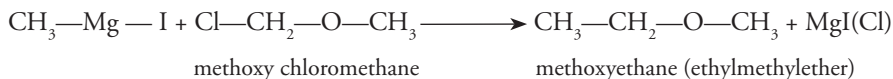
6. **Synthesis of esters with chloroacetic ester**

Grignard reagents react with chloroacetic ester to give higher esters.



7. **Synthesis of ethers (alkoxyalkanes) with chlorinated ethers**

Chlorinated ethers react with $R-MgX$ to give higher ethers.



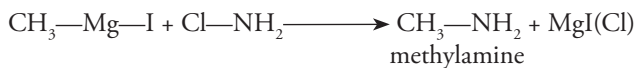
8. **Synthesis of cyanoalkanes with cyanogen chloride**

Alkyl cyanides can be obtained by the action of cyanogen chloride on $R-MgX$.



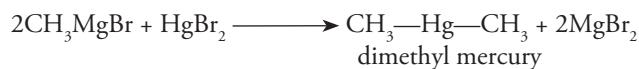
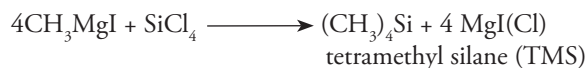
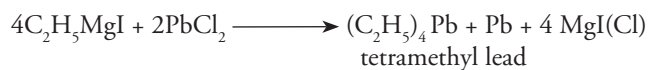
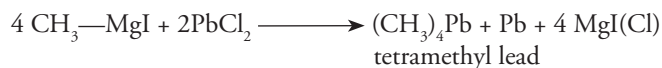
9. **Synthesis of primary amines with chloramine ($\text{Cl}-\text{NH}_2$)**

Chloramine reacts with $R-MgX$ to form primary amines.



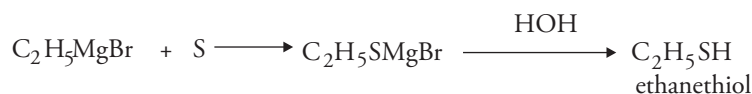
10. **Synthesis of other organo-metallic compounds with metal halides**

Grignard reagents yield other organo-metallic compounds with corresponding metal halides, as shown below:



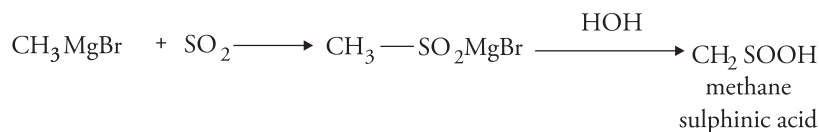
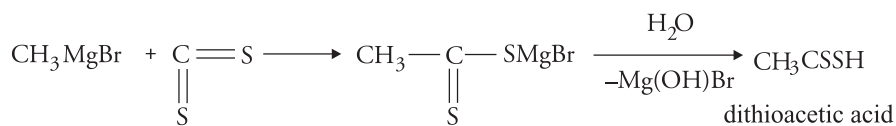
11. Synthesis of thiols

Thioalcohol (thiols or mercaptans) are obtained by the hydrolysis of the adducts of Grignard reagents with sulphur.



12. Some others synthesis

Grignard reagents react with halogens, oxygen, carbon disulphide, sulphur dioxide and so on, to give varied products as shown below



Summary

- Organometallic compounds are those compounds which possess a metal carbon bond $M^{\delta+} - C^{\delta-}$. However, all compounds with metal carbon bond are not organometallics.
- Organometallic compounds are classified on the basis of nature of metal carbon bond as ionic and covalent compounds. Covalent compounds can be σ bonded, π bonded or bridged.
- Organometallic compounds can be prepared by the direct reaction of metal with organic group, hydrometallation, transmetallation and metallation reaction.
- Organometallic compounds find use in catalysis and polymerisation reactions.
- Grignards reagent ($R MgX$) are of the immense utility and can be used to prepare various organic compounds.

Important Dates in Organometallic Chemistry

- 1912 Nobel Prize for Victor Grignard and Paul Sabatier.
- 1930 Henry Gilman works on lithium cuprates
- $$RX + 2Li \longrightarrow RLi + LiX$$
- 1951 Ferrocene is discovered
- 1963 Nobel Prize for K. Ziegler and Giulio Natta on Ziegler–Natta catalyst
- 1965 Discovery of cyclobutadiene iron carbonyl $(C_4H_4)Fe(CO)_3$
- 1968 Heck reaction discovery
- 1973 Nobel Prize for G. Wilkinson and E.O Fischer on sandwich compounds
- 2005 Nobel Prize for Y. Chauvin, R Grubbs and R. Schrock on metal catalysed alkene metathesis
- 2010 Nobel Prize for Richard F Heck, Ei-ichi. Negishi, Akiva Suzuki ‘for palladium catalysed cross couplings in organic synthesis’

Review Questions

1. What are organometallic compounds? Classify them.
2. Explain the various methods of preparation of organometallic compounds.
3. Explain the application of organometallic compounds in the following:
 - (i) Hydrogenation of alkenes
 - (ii) Hydroformylation of alkenes.
 - (iii) Synthesis of acetic acid
 - (iv) Polymerisation of alkenes

4. Starting from a suitable Grignard reagent how will you obtain
 - (a) a primary alcohol
 - (b) a secondary alcohol
 - (c) a tertiary alcohol
 - (d) an aldehyde
 - (e) a ketone
 - (f) a carboxylic acid
 - (g) TMS
 - (h) an ester
 - (i) a thiol and
 - (j) acetonitrile
5. How is ethyl magnesium iodide prepared? What precaution must be observed in this preparation?
6. What is Grignard reagent? How will you obtain the following compounds from a Grignard reagent?
 - (a) propane
 - (b) ethanol
 - (c) 2-methyl-2-propanol
 - (d) 2-propanol
 - (e) propanone
 - (f) ethanal
 - (g) ethyl propanoate
 - (h) ethoxyethane
 - (i) ethanoic acid
 - (j) cyanoethane
7. How will you obtain the following using Grignards reagent
 - (a) propanone from methane
 - (b) ethanoic acid from carbon dioxide
 - (c) ethanol from methanal
 - (d) ethane from ethanoic acid
 - (e) ethanol from methanol

Multiple Choice Questions

1. Which of the following is not an organometallic compound
 - (a) $(C_2H_5)_2Zn$
 - (b) $(C_2H_5)_2Fe$
 - (c) $Ni(CO)_4$
 - (d) $B(OCH_3)_3$
2. Which of the following is a sigma bonded organometallic compound
 - (a) Ferrocene
 - (b) Grignard's reagent
 - (c) Zeise's salt
 - (d) Nickel carbonyl
3. Which of the following is not a π bonded organometallic compound
 - (a) $(C_5H_5)_2Fe$
 - (b) $(C_6H_5)_2Cr$
 - (c) C_5H_5K
 - (d) $K[PtCl_3(C_2H_4)]$
4. Chemically Zeise's salt is
 - (a) $K[PtCl_3(C_2H_4)]$
 - (b) CH_3MgBr
 - (c) CH_3Zn
 - (d) $(C_6H_5)_2Cr$
5. Wilkinson's catalyst is widely used for
 - (a) Dehydrogenation of alkynes
 - (b) Homogeneous hydrogenation of alkenes
 - (c) Hydroformylation
 - (d) Heterogeneous hydrogenation of alkenes

6. Catalyst which is widely used in heterogeneous catalysis is
(a) Wilkinson catalyst (b) Zeigler Natta catalyst
(c) Rhodium carbonyl iodide (d) Octa carbonyl dicobalt
7. Which of the following reacts with Grignard's reagent to produce primary alcohol
(a) Formaldehyde (b) Acetaldehyde
(c) Formic ester (d) Ketones
8. Name the product formed when Grignard's reagent react with carbon dioxide and the adduct is hydrolysed
(a) Alcohols (b) Acids
(c) Aldehydes (d) Esters
9. $\text{CH}_3\text{MgI} + \text{CH}_3\text{CHO} \rightarrow \text{A}$. A is
(a) 1-propanol (b) 2-butanol
(c) 2-propanol (d) butylalcohol
10. Grignard's reagent react with compounds containing active hydrogen to evolve-
(a) Methane gas (b) Ethane gas
(c) Does not react with such compounds (d) Both the above

Solution

- | | | | | | | |
|-------|-------|--------|-------|-------|-------|-------|
| 1 (d) | 2 (b) | 3 (c) | 4 (a) | 5 (b) | 6 (b) | 7 (a) |
| 8 (b) | 9 (c) | 10 (a) | | | | |

Chapter 22

Green Chemistry

22.1 Introduction

From the onset of human civilisation, man has worked continuously to make his life comfortable. Chemistry has played a vital role in improving the quality of human life. Gone are the days when man wandered for food, travelled on bullock cart, used pigeons to send messages and depended on conventional treatment methods for his well-being. Sophisticated cultivation techniques, advanced means of transport, postal services, telegraph and now mobile and the internet have replaced the older methods, and medical science has grown tremendously. However, all this has endangered our environment, our health and our non-renewable natural resources.

Let us consider a small example. When man learnt to cultivate, he depended on nature for growing crops. Sometimes, he lost his crops to diseases and at other times, to the invasion of insects and pests. His yield was less. As he gradually acquired knowledge, he developed pesticides to fight against pests and diseases; he developed inorganic fertilisers which increased the yield of crops drastically. High yielding varieties were discovered, but the use of pesticides, herbicides, nitrogenous fertilisers have led to ground water pollution by the leaching of these chemicals into the ground. Occurrence of pesticide residues in food products, fertiliser run off from fields leading to eutrophication are the adverse effects of using pesticides and fertilisers. Hence, the discovery and use of these products have increased the potential risk to human health and environment.

Similarly, the use of refrigerators and air conditioners for a comfortable living has adversely affected the environment due to the emission of chlorofluorocarbons. These CFCs have led to the depletion of the ozone layer which filtered the ultraviolet radiations of the sun causing cancers. All the above can be attributed to the growth and contribution of chemistry. Now, while environmental chemistry seeks to study the role and effect of pesticides, herbicides and chlorofluorocarbons in the environment and also seeks measures to mitigate their effects, green chemistry addresses environmental concerns at the molecular level. It aims to design procedures that can reduce the production of waste, promote the efficient use of the raw material, design pesticides and herbicides that will not contaminate food products and will not cause ground and water pollution.

Let us consider another example. The use of polythene bags is increasing tremendously. Its adverse effects are many and have caused concern among the international community. An environmental chemist will study the effects of polythene bags on land, soil, water and environment at large,

whereas a green chemist will work in the direction of developing polythene that is eco-friendly. She will try to develop biodegradable plastic bags that release less toxic chemicals after degradation. In other words, she works to reduce the potential risks to the environment. Hence, green chemistry helps in developing methods that help to eliminate hazardous waste from the environment and maintain a clean, benign environment and promote sustainable growth. It is because of this that green chemistry is also termed as *benign chemistry* or *sustainable chemistry*.

Green chemistry is a tool that aims at focusing on all the steps involved in product generation and tries to optimise the use and generation of hazardous chemicals. It is concerned with the development of chemical technology and processes that do not cause pollution. IUPAC has defined green chemistry as follows.

‘The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances’.

(Source: IUPAC, *Pure and Applied Chemistry*, 2000. Vol. 72, No 7, PP 1207–1228)

22.2 Emergence of Green Chemistry

The science of green chemistry is new and dates back to the early 1990s. Public awareness about the hazards of pesticides, pollution and increasing use of chemicals was created by *Silent Spring* authored by Rachel Carson, writer, biologist and environmentalist in 1962. After her work, people became concerned about the potential hazards of the use of chemicals and this created pressure on industry to develop an eco-friendly pathway for the synthesis of chemicals. The Office of Pollution Prevention and Toxics of the United States Environment Protection Agency founded the Alternative Synthetic Pathway Program in 1991 and paved the way for the origin of green chemistry.

The first book on green chemistry titled *Benign by Design, Alternative Synthetic Design for Pollution Prevention*, was authored by Paul T Anastas and Carol A Farris in 1994. However, the term ‘green chemistry’ began to be used only between 1996 and 1997. After the year 1996, IUPAC involved itself in the field of green chemistry and since then, various organisations and institutes have been set up to promote green chemistry. In the present scenario where the use of chemicals cannot be avoided, green chemistry becomes significant as it paves the way for clean and sustainable growth. Green chemistry is based on 12 basic principles which we will discuss now.

22.3 Twelve Principles of Green Chemistry

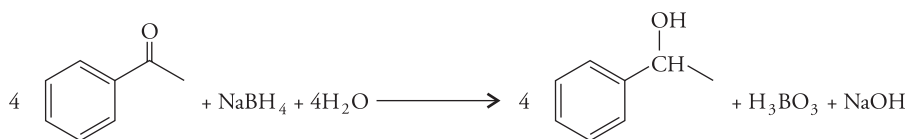
1. **Prevention** Avoiding or reducing waste generation is the first step in pollution prevention. The use of fossil fuel generates greenhouse gases like CO_2 and CH_4 . Instead of treating CO_2 after production, green chemistry underlines the need to develop techniques that can reduce the production of CO_2 at source. This can be done by the use of renewable energy sources like solar energy, wind energy, CNG, etc.

Similarly, the disinfection of water by chlorination generates harmful chlorinated compounds which pollute the environment. This can be prevented by using a green oxidant like ozone or potassium permanganate.

2. **Atom economy** This concept was developed by Barry Trost of Stanford University (USA). He was awarded the Presidential Green Challenge Award in 1998 for his work. This principle emphasises the need to incorporate maximum number of reactant molecules in product formation. Atom economy is a measure of the percentage of reactant atoms leading to product formation. Most reactions have a yield of about 70–90%. The atoms that are not incorporated in the product result in the generation of waste.

$$\text{Percentage atom economy} = \frac{\text{Formula weight (FW) of the desired product}}{\text{Formula weight (FW) of all reactants}} \times 100$$

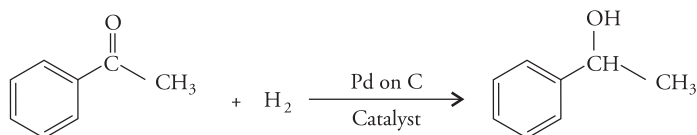
Consider the reduction of ketone to secondary alcohol using sodium boron hydride as the reductant.



Reagent formula	Reagent FW	Utilised atoms
1. C ₈ H ₈ O	120 × 4 = 480	C ₈ H ₁₀ O
2. NaBH ₄	38	
3. H ₂ O	18 × 4 = 72	
Total	590	122 × 4 = 488

$$\text{Percentage atom economy} = \frac{488}{590} \times 100 = 82.70\%$$

Hence, nearly 17.3% of the reactant atoms is wasted in unwanted side products. Green chemistry envisages a better atom economy which can be achieved by an alternative reaction pathway. If molecular hydrogen is used as a reducing agent in the presence of palladium and charcoal as a catalyst, then the atom economy rises to 100% and there is no generation of waste.



$$\text{Weight of all the reactants} = 120 + 2 = 122$$

$$\text{Weight of utilised atom} = 122$$

$$\text{Atom economy} = \frac{122}{122} \times 100 = 100\%$$

3. **Less hazardous chemical synthesis** Green chemistry aims at adopting those synthetic procedures which use and produce substances which are not toxic or hazardous and do not harm living organisms and the environment.
4. **Designing safer chemicals** Chemical products should be designed in such a way that they achieve their desired goal without creating any hazardous or toxic effects. For this, it is essential to study the structure of the compound and analyse which part gives the required property and which part is responsible for toxicity. Toxicity can then be reduced by bringing about suitable changes in that part. For example, chlorofluorocarbon causes ozone depletion due to the release of chlorine radical in the upper atmosphere. To prevent this, chemists have designed a new compound, hydrofluorocarbon, in which the chlorine group is replaced by hydrogen. The ozone depletion potential of this new compound is far less than the ozone depletion potential of chlorofluorocarbons.
5. **Use of safer solvent and auxiliaries** Solvents and auxiliaries play a vital role in chemical reactions. They are used for the purification and separation of substances (for example, chromatography techniques). They are required in large volumes and are generally volatile and toxic in nature. For example, carbon tetrachloride and benzene commonly used as solvents are carcinogenic; various cleaning products like paints use solvents that are highly volatile and toxic. Green chemistry emphasises the need to avoid unnecessary use of solvents and wherever essential, they should be innocuous (harmless).
6. **Design for energy efficiency** Chemical reactions generally require a lot of energy. Preparation of cement, glass and other chemicals requires high temperature (1600–1800 °C). This energy generally comes from the use of fossil fuels. Green chemistry emphasises the development of such chemical procedures that can be carried out at room temperature and pressure.
7. **Use of renewable feedstock** Green chemistry emphasises the need to use raw material that is renewable. For example, electricity is generated by burning coal which is non-renewable and a depleting raw material. Instead of coal, a green chemist would suggest the use of renewable feedstock like agriculture waste (bagasse, rice husk, biomass, municipal solid waste, etc), solar energy, etc.
8. **Reduce derivatives** Green chemistry avoids adding extra steps and modification of chemical processes as these require additional reagents and can generate extra waste. When a chemical reaction is to be carried out selectively at one site in a multifunctional compound, then the other groups are temporarily blocked by protecting groups. After the reaction is over, these groups are again released by using suitable solvents. Such procedures require additional steps and the use of extra solvents. Green chemistry envisages the development of synthetic routes where unnecessary derivatisation (use of blocking groups, protection/de-protection) can be avoided.
9. **Use of catalyst** Use of selective catalysts increases the specificity of the reaction and reduces the formation of by products. A catalyst lowers the activation energy of the reaction, thereby reducing the energy consumption. Their role should be like that of living organisms who play their role and then mingle harmlessly in the ecosystem.
10. **Design for degradation** Chemical substances should be designed in such a way that they degrade in the environment to give harmless end products. Plastics ordinarily do not

decompose in landfills. Designing biodegradable plastics can help reduce land and soil pollution.

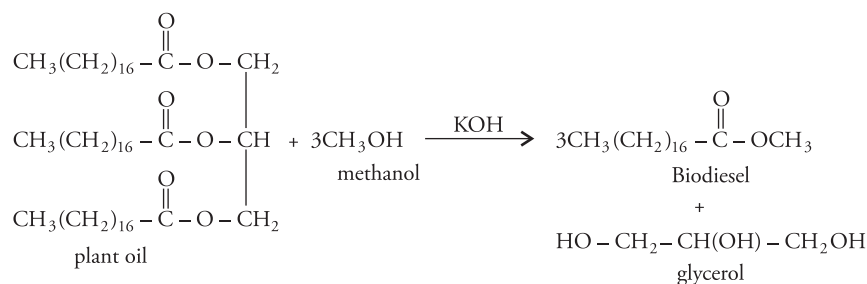
11. **Analysis in real time to prevent pollution** Chemical reactions and procedures should be monitored during the progress of the reaction to detect the formation of any unwanted and toxic products. Analytical methods should be adopted to allow process monitoring and control and minimise the formation of toxic substances.
12. **Inherently safer chemicals for accident prevention** Chemicals should be designed in such a way that they do not cause severe accidents like explosions or fire in case of accidental release. The design should be such that in case of accidental release, they convert to non-toxic products and escape safely into the atmosphere.

It is evident that the above-mentioned principles encompass the concept of sustainability. Some important areas which utilise the principles of green chemistry are discussed in the forthcoming sections.

22.4 Use of Alternative Feedstock (Biofuels)

Feedstocks are raw materials that are converted into products. Generally, three types of materials serve as feedstock: (a) Fuel used to provide heat energy, (b) raw materials and (c) solvents used for the extraction of raw materials.

The extent of waste production, nature of the waste, by products and usage of energy depends upon the selection of feedstock. An ideal feedstock should be renewable and should not pose any potential hazards. It should be converted into final products in a few steps with 100% atom economy and 100% yield. Most feedstocks are derived from petroleum products which are a mixture of hydrocarbons. To be used as feedstocks, these hydrocarbons have to be oxidised and separated one by one. This requires energy and the use of hazardous chemicals. The greener way is to use renewable feedstocks. For example, solar energy and energy from biomass can be used as fuel; biodiesel derived from vegetable oils and wasted plant oils is also a very promising source of energy.



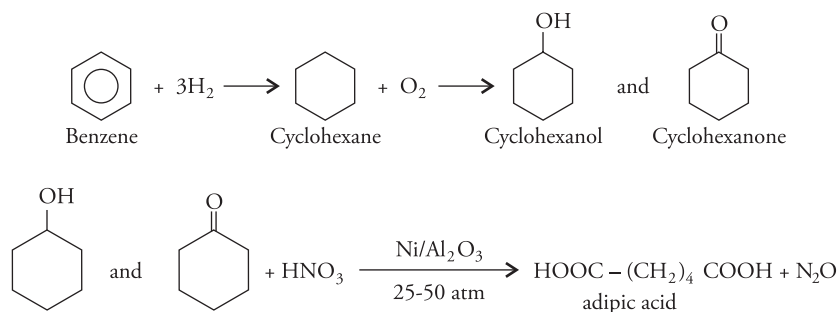
Vaseline, lubricants and polymers are generally obtained from petroleum products. These products can be obtained by utilising plants as feedstocks. The products obtained by the use of these renewable feedstocks are more benign and have less side effects.

Waste biomass can be used as chemical feedstock in many industries. This will help to reduce the problem associated with their disposal in landfills. The cellulose available in waste biomass can be converted enzymatically into glucose which can further be converted to ethanol (used as a fuel) by the action of enzymes.

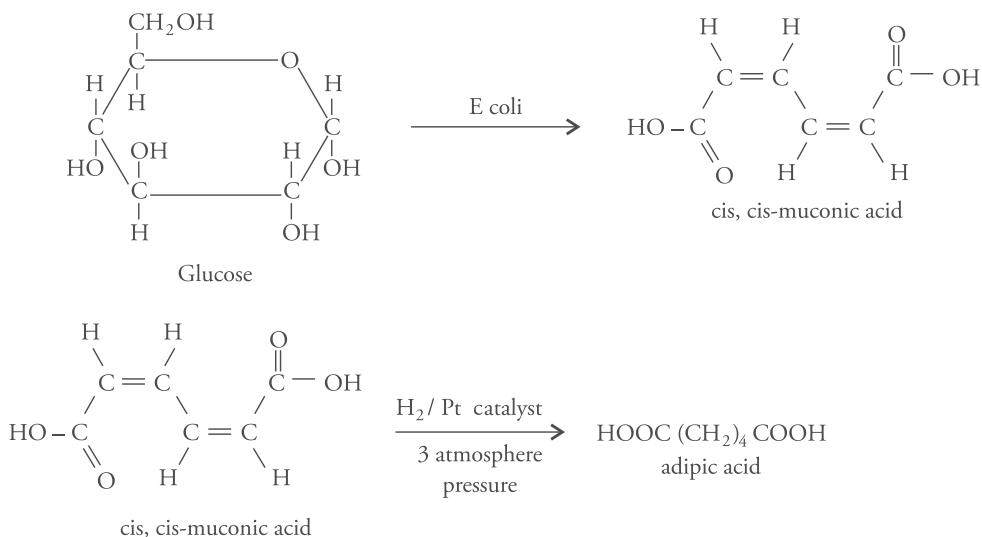
Similarly, adipic acid used for the manufacture of nylon is conventionally prepared from the petroleum product, benzene (a carcinogenic compound). Benzene is oxidised to cyclohexanol and cyclohexanone which on further oxidation with nitric acid in the presence of $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst at 25–30 atm pressure yields adipic acid feedstock. This method not only uses benzene (a hazardous volatile compound), it also produces N_2O that causes significant environmental problems.

Adipic acid can be synthesised by using an alternative renewable feedstock, glucose, which on hydrogenation in the presence of genetically modified *Escherichia coli* bacteria yields cis, cis-muconic acid. This acid converts to adipic acid when reduced with hydrogen at 3 atm pressure in the presence of platinum catalyst.

Conventional method of synthesis of adipic acid

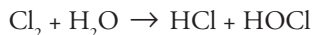


Green synthesis of adipic acid

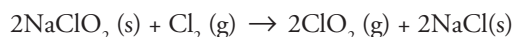


22.5 Use of Innocuous Reagents

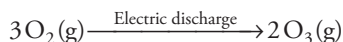
Principles of green chemistry guide us to make use of innocuous or less harmful reagents for synthesis of chemicals. For example, water is generally disinfected by a municipality using potentially hazardous chlorine gas. The reaction occurs as follows.



HOCl is a good disinfecting agent as it kills bacteria and virus by inactivating their enzymes. However, the use of chlorine gas poses a danger by the formation of undesirable trihalomethanes. This problem is overcome by the use of ClO_2 which although a very good disinfectant, is at the same time, dangerously reactive and unsafe to store and transport. Hence, it is prepared in small quantities on the site.



Instead of using dangerous chemicals like Cl_2 and ClO_2 for water disinfection, green chemistry endorses the use of an innocuous reagent like ozone for water disinfection.



The raw material is air from which ozone can be produced as required.

Similarly, in paper, pulp and textile industry, toxic chlorine gas is used for bleaching. This can be replaced by a benign bleaching agent like H_2O_2 under suitable conditions.

The Friedel–Crafts alkylation and acylation reactions catalysed by Lewis acid like aluminium chloride lead to the formation of waste products. This can be avoided by the use of solid catalysts like zeolites which are highly selective and avoid the formation of by products.

22.6 Use of Alternative Solvents

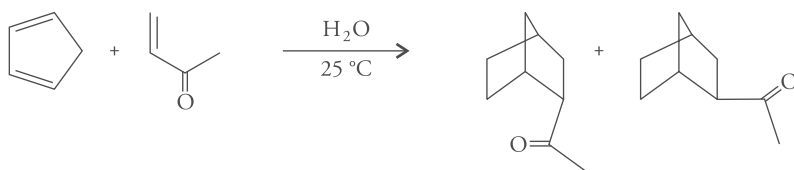
Solvents play a very important role in most chemical reactions. They serve as a medium in which the reagent molecules can dissolve and undergo reaction. Substances used as solvents are generally volatile and are used in large volumes. The commonly used solvents are carbon tetrachloride, benzene, chloroform and perchloroethylene. These are carcinogenic and many hydrocarbon solvents have neuro toxicological effects. Apart from having a direct effect on human beings, most solvents have adverse environmental implications too. Since they are used in large volumes, they are drained out into water bodies or land where they cause land and soil pollution. In water bodies, they adversely affect the aquatic flora and fauna.

Volatile organic compounds used as solvents for cleaning, in paints and various organic chemical reactions escape into the environment and cause global warming. They also have the potential to elevate the ground level ozone in the atmosphere. Moreover, these solvents are highly inflammable, combustible, and explosive and can cause serious accidents. In the light of the above hazards of

solvents, green chemistry suggests the use of alternative solvents. Some common alternate green solvents are

- Water
- Supercritical fluids like carbon dioxide
- Ionic liquids
- Solvent-free processes
- Bio solvents

1. **Water** Water is the ultimate green solvent. It is non-toxic, naturally occurring and non-volatile, inexplusive and non-inflammable. In many cases, the use of water as a solvent increases the rate of the reaction. For example, the Diels–Alder reaction of cyclopentadiene and butenone in water is about 700 times faster than in any other organic solvent. If LiCl is added to this aqueous phase, the rate of reaction increases 1800 times.



2. **Supercritical water (SC H₂O)** At a temperature of 647 K and pressure of 218 atm, water becomes ‘supercritical’. The hydrogen bonds of water are broken and it acquires the ability to dissolve organic solvents like paraffins, aromatics, etc., which were otherwise insoluble in it. Supercritical water has increased acidity and lower polarity that increases its application to organic reactions. The synthesis of quartz crystal used in mobile phones using SC water as solvent is an excellent achievement. The technique of supercritical water oxidation (SCWO) is used in the separation processes to treat toxic waste water.
3. **Supercritical carbon dioxide (SC CO₂)** CO₂ is a non-toxic, non-inflammable gas at ambient conditions. It has a low critical temperature of 304 K and pressure of 74 atm. SC CO₂ can dissolve non-polar compounds and some polar compounds like methanol, acetone, etc. It also dissolves tetrahydrofuran, vinyl monomers, azo and peroxy initiators. However, ionic compounds, water and many polymers are insoluble in it. SC CO₂ is an alternative medium for carrying out oxidation reactions.

Other reactions that use SC CO₂ as a solvent are given below.

- Polymerisation of tetrafluoroethylene using fluorinated initiators
 - Used for dry-cleaning, metal cleaning and textile processing in place of traditional organic solvents. Liquid CO₂ finds use in the microelectronic industry to spin-coat photoresists.
 - SC CO₂ is used to clean integrated circuits and flat panel displays during manufacturing in place of water and organic solvents.
4. **Room temperature ionic liquids** These solvents consist entirely of ionic species and are often fluid at room temperature. Because of their ionic nature, they do not have a measurable vapour pressure and hence do not emit volatile organic compounds. These solvents consist of an anion and a cation and their properties can be adjusted to suit the

requirements of a particular process. Hence, these solvents are termed as *designer solvents*. By making simple changes in the structure of their ions, their properties like melting point, viscosity, density and hydrophobicity can be varied. The first room temperature ionic liquid $[\text{EtNH}_3][\text{NO}_3]$ with a melting point of 12 °C was discovered in 1914. Later on, binary ionic liquids made from a mixture of aluminium (III) chloride and N-alkylpyridinium or 1, 3-dialkylimidazoliumchloride were discovered. The chloroaluminate (III) ionic liquids obtained by mixing organic halide salt with aluminium (III) chloride, are used in

- Friedel–Crafts reaction instead of Lewis acids.
 - Acylation reactions for the manufacture of various fragrance molecules of commercial importance.
 - Cracking and isomerisation reactions.
 - Catalytic hydrogenation reactions of cyclohexene using Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$.
5. **Solvent-free reactions** Reactions carried out without the use of solvents are greener as there is no problem of disposal of solvent, evaporation of solvents, etc. These reactions are carried out either in solid state or on solid surfaces like clay, zeolites, silica, alumina, etc. Reactions like aldol condensation, Michael addition and Stobbes condensation have been carried out successfully in solid state (solvent-free environment). Aldol condensation is carried out by grinding together solid sodium hydroxide with benzaldehyde and acetyl pyridine. The product is also formed in the solid state.
6. **Use of bio solvents** Bio-solvents derived from crops are biodegradable, easy to recycle, non-ozone depleting, non-corrosive and non-carcinogenic. They are green solvents. Ethyl lactate derived from processing corn is an example of a very commonly used green solvent. It is the ester of lactic acid and finds use in paints and coating industry. It has replaced hazardous solvents like acetone, xylene and toluene.

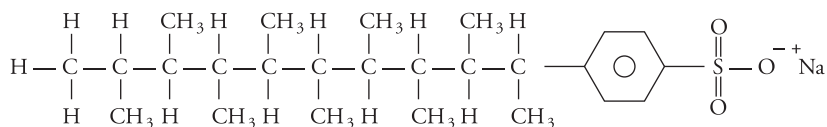
22.7 Design of Safer Chemicals

Green chemistry aims at designing chemicals that are eco-friendly and degrade safely after their use. They do not adversely affect living organisms. This is done by analyzing the structure and activity relationship of the compound and identifying the part of the molecules that gives the desired products and the part that is responsible for toxic effects. After this analysis, the molecules can be re-designed by

- Replacing the toxic functional group by a less toxic one.
- If it is not possible to substitute the toxic functional group, then its toxicity can be masked using a non-toxic group so that only the desired functional group is released.
- The bio availability of molecules can be modified by manipulating its properties like stability, water solubility, lipophilicity, etc., so that the molecule does not reach the target where its toxicity is pronounced. This can be understood with the help of the example of chlorofluorocarbons (CFCs). The CFCs reach the stratospheric ozone layer and release Cl which causes depletion of the ozone layer. Therefore, a safer chemical hydrofluorocarbon was

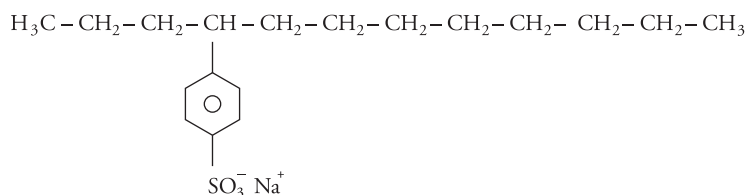
designed which although has the potential to deplete ozone is unable to reach the stratosphere as it breaks down in the troposphere.

- For a clean environment, it is necessary to design chemicals that can degrade safely in the environment without releasing toxic end products. This solves the problem of their disposal. Design of biodegradable plastic is an example of the above type. Detergents in sewage were a problem since they were degraded very slowly by bacteria.



Branched chain alkyl benzene sulphonate (non-biodegradable)

This problem was solved by designing another compound, linear alkyl sulphonate, which is readily biodegradable.

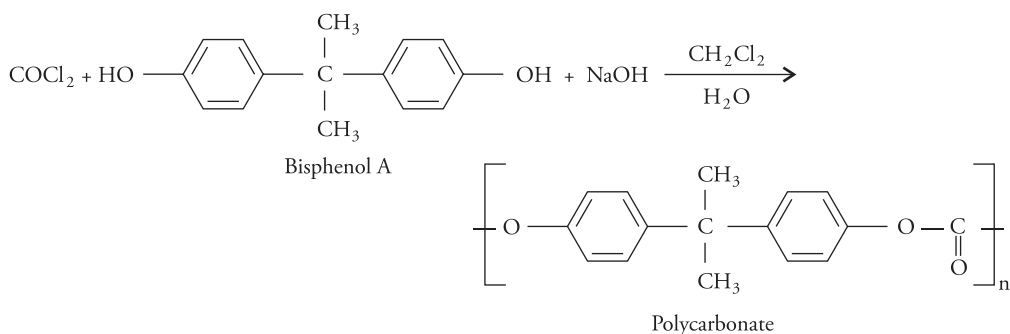


Linear alkyl benzene sulphonate (biodegradable)

22.8 Designing Alternative Reaction Methodology

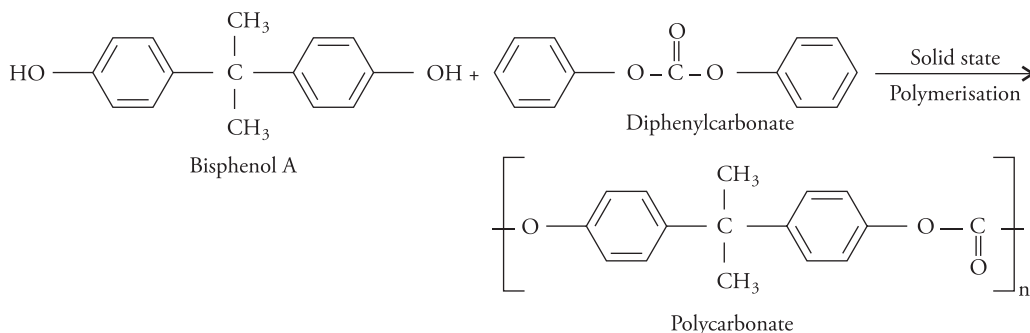
A reaction pathway that uses and generates less toxic by products should be adopted.

Synthesis of polycarbonate The traditional route for the synthesis of polycarbonate polymer used phosgene (COCl_2) which is very toxic. A poisonous solvent CH_2Cl_2 is formed and it is difficult to separate the product from this solvent.



Traditional route for the synthesis of polycarbonate

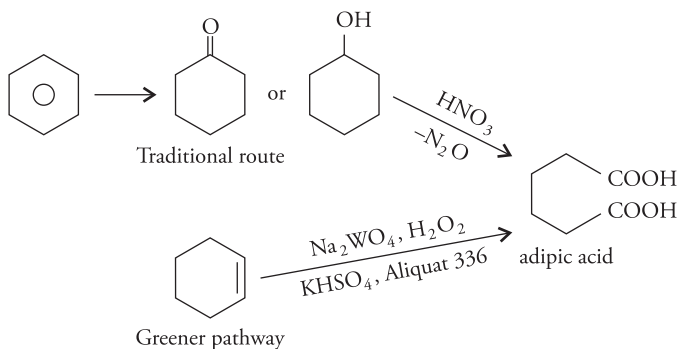
The greener route does not use phosgene and CH_2Cl_2 is also not formed.



Green pathway for polycarbonate synthesis

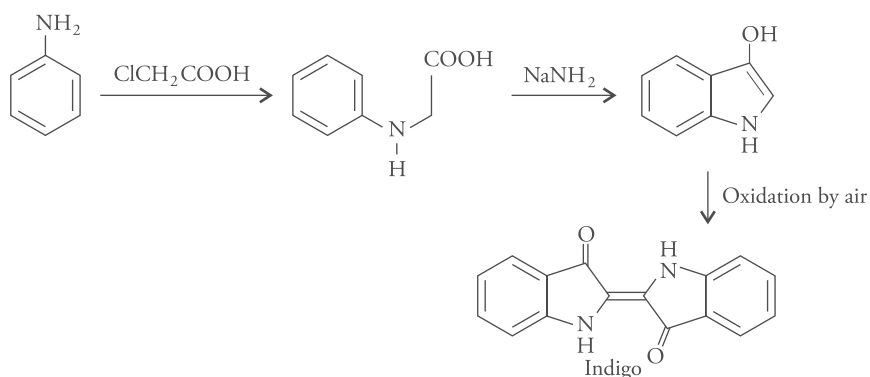
Synthesis of adipic acid

As discussed in Section 22.4, the conventional method for the synthesis of adipic acid uses carcinogenic benzene. The greener synthesis can utilise glucose as a feedstock. The most commonly used green procedure for synthesis of adipic acid uses cyclohexene as the starting reagent. It is oxidised with 30% hydrogen peroxide (H_2O_2). Sodium tungstate Na_2WO_4 dissolved in a special organic solvent (Aliquat 336) is used as a catalyst.

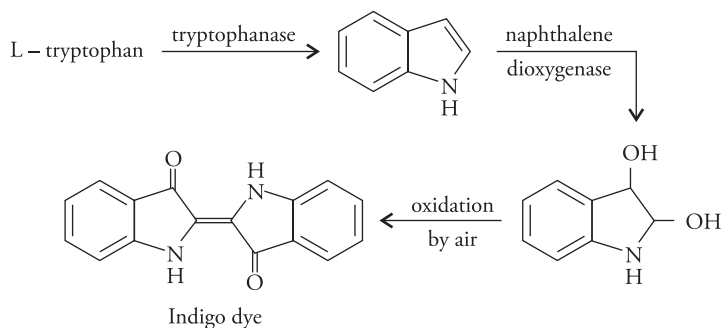


(Aliquat 336 is a quarternary ammonium salt used as an important phase transfer catalyst. It is methyl trioctyl-ammonium chloride (C_8H_{17})₃ $\text{N}^+\text{CH}_3\text{Cl}^-$).

Synthesis of indigo dye The traditional pathway for synthesis of indigo dye uses toxic aniline as a feedstock.



In the green pathway, the feed stock is L-tryptophan, a renewable material of plant origin.



22.9 Minimising Energy Consumption

Microwave and ultrasonic radiation assisted green synthesis Chemical reactions generally use thermal sources of energy derived from fossil fuels. This energy is non-specific and does not directly attack the bonds or chemicals undergoing the reaction. A large portion of the energy goes into heating the reactor, solvents or is dissipated into the environment.

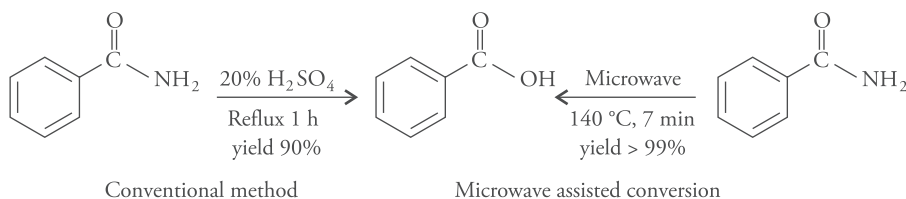
In order to reduce the hazards caused by the use of conventional sources of energy, these days microwave and ultrasonic radiation assisted chemical reactions are carried out. These methods are safe, energy-efficient, clean and increase the rate of the reaction.

Use of microwave in synthesis

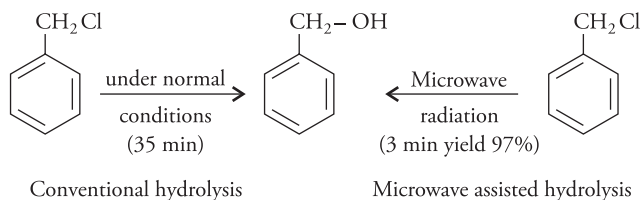
The use of microwave radiation for synthesis dates back to 1986. Since then, a large number of reactions have been investigated and carried out safely using these radiations. Microwave assisted synthesis requires less energy, generates less waste and avoids the use of solvent. They are cleaner and eco-friendly with a high product yield and minimum waste. The reaction occurs at a very fast rate. The commonest example of the use of microwave assisted radiation in day-to-day life is in the kitchen. These days, microwave cooking is replacing cooking using conventional fuels because it is fast and saves time and energy.

Microwave assisted organic reactions

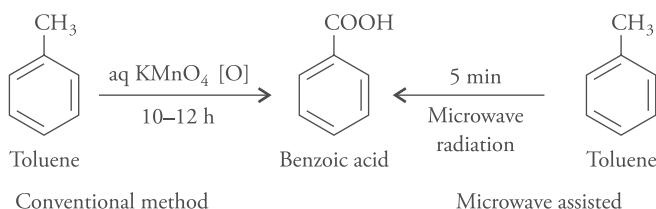
- Hydrolysis of benzamide** In the hydrolysis of benzamide, the use of conventional heat source requires refluxing with 20% H_2SO_4 for one hour and the yield is 90%. The same conversion if carried out in microwave, can be achieved by 7 min microwave radiation at 140°C and the yield is 99%.



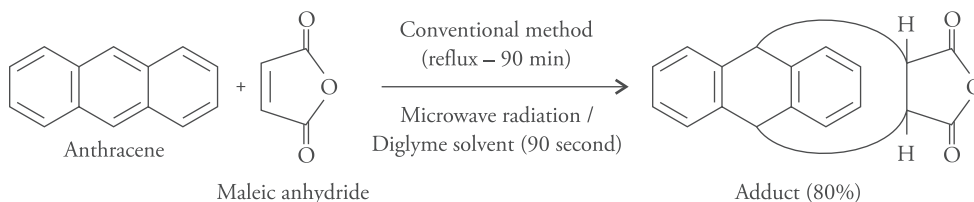
2. **Hydrolysis of benzyl chloride** Normal hydrolysis of benzyl chloride takes 35 min, whereas the same reaction can be completed in just 3 min with an yield of 97% in the presence of microwave radiations



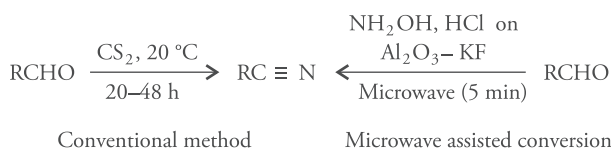
3. **Oxidation of toluene to benzoic acid** Conventional method of oxidation in the presence of KMnO_4 usually takes place in 10–12 h. However, under the influence of microwave radiations, the reaction is completed in just 5 min and the yield is much better.



4. **Diels–Alder reaction** Anthracene (a diene) and maleic anhydride (a dienophile) form an adduct on refluxing in nearly 90 min. The same reaction can be completed in just 90 s in the presence of microwave radiations.



5. **Conversion of aldehydes to nitriles** Conventional method using CS_2 is completed in 20–48 h at about 20°C , whereas the same reaction is completed in just 5 min in the presence of microwave radiations.



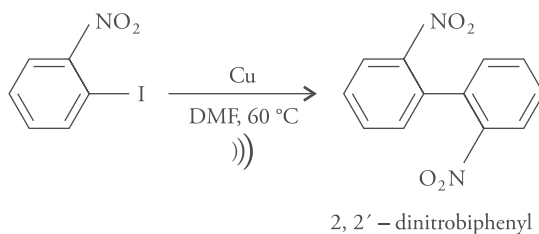
Use of ultrasound radiation in synthesis

Ultrasound radiations (20 kHz to 1 MHz) are very high energy radiations. These waves propagate through the liquid medium by a series of compression and rarefaction cycles, and make the particles of the medium oscillate about their mean position. During the compression phase, the liquid molecules come close to each other and vice versa. Bubbles are produced inside the liquid

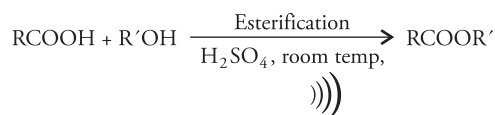
irradiated with ultrasound radiations and under appropriate conditions, these bubbles collapse violently and generate very high temperature (5000 °C) and pressure (over 1000 atmosphere). This effect is called cavitation and the chemical reaction is initiated because of this cavitation effect. The cavitation effect of ultrasound radiations breaks solids into small pieces, thereby increasing their surface area. The study of chemical reactions under the influence of ultrasound radiations is called sonochemistry. The symbol [] is used to depict ultrasound assisted reactions. Ultrasound assisted reactions are performed in specially designed apparatus in which sound waves are generated using electrical energy.

Some common reactions are given below.

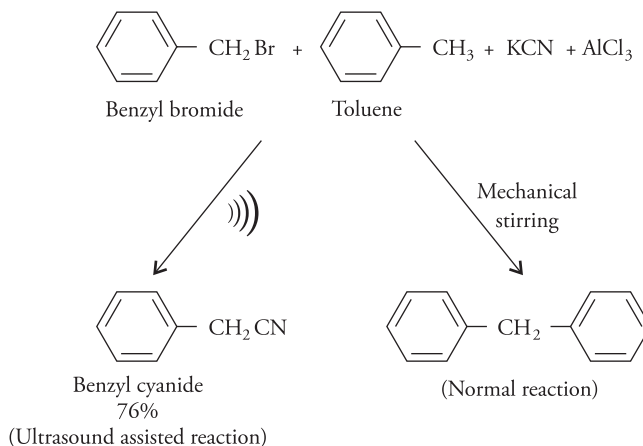
1. **Ullman reaction** It is the coupling of two molecules of iodobenzene in the presence of copper powder in a sealed tube to form biphenyl. The reaction takes place at high temperature and the yield is also low. In the presence of ultrasound radiation, the rate of reaction and the yield both increase significantly. It is believed that the ultrasound radiations break the copper catalyst increasing its surface area.



2. **Esterification** If the reaction is carried out by conventional methods, it proceeds slowly with poor yields. However, in the presence of ultrasound radiations, the reaction occurs at room temperature with better yield.



3. **Sonochemical switching** Sometimes in the presence of ultrasound radiations, the reaction pathway changes.



Ultrasound radiations can also be used for the following.

- Surface cleaning without the use of surfactants: The dirt is eroded by ultrasound radiations. Very soon, the market will have washing machines which clean without using water.
- Emulsification without the use of emulsifying agents: The high frequency ultrasound radiations help in the dispersion of the dispersed phase.
- Purification of water where some water pollutants like chlorinated esters can be destroyed sonochemically.
- Ultrasound radiations are extensively used in industry for welding, cutting, solvent de-gassing, cell disruption, atomisation and extraction of substances.

Summary

- Green chemistry aims at developing chemical reactions that would not use or generate toxic chemicals. It is also termed as benign chemistry or sustainable chemistry.
- It is based on 12 principles which enshrine the motto, 'prevention is better than cure'. The principles of green chemistry emphasises pollution prevention, atom economy to reduce generation of waste, design of safer chemicals, use of solvents that are natural and innocuous, promotes the use of renewable feedstock, production of products that do not leave hazardous products after use and are biodegradable. It also emphasises energy efficient reactions.
- Atom economy

$$= \frac{\text{Formula weight of desired products}}{\text{Formula weight of all the reactants}} \times 100$$

- Microwave assisted reactions are those in which microwave radiations assist the reaction. These reactions require less energy, generate less waste and avoid the use of solvent.
- Reactions assisted by ultrasound waves also occur rapidly under normal reaction conditions. They are termed as sonochemical reactions.

Review Questions

1. What is green chemistry? Discuss the twelve principles of green chemistry.
2. Green chemistry is also called benign chemistry or sustainable chemistry. Comment.
3. What do you understand by atom economy? How does atom economy help in waste reduction?
4. Write short notes on
 - (i) Use of alternative feedstocks
 - (ii) Use of innocuous reagents

5. The use of hydrocarbon solvent has toxic effects on living organisms and the natural environment. Suggest some suitable green alternatives and explain how they function.
6. What are room temperature ionic liquids and supercritical liquids? Explain their role in green synthesis.
7. How can we design safer chemicals for prevention of environment pollution? Explain with the help of suitable examples.
8. Explain the traditional and green methods for the synthesis of the following chemicals.
 - (i) Adipic acid
 - (ii) Polycarbonate
 - (iii) Indigo dye.
9. Discuss the role of microwave radiations and ultrasound radiations in green chemistry.

Multiple Choice Questions

1. Which term is not used for green chemistry?
 - (a) Sustainable chemistry
 - (b) Benign chemistry
 - (c) Environmental chemistry
 - (d) Clean chemistry
2. Which is not a principle of green chemistry?
 - (a) Prevention is better than cure
 - (b) Removal of waste after generation
 - (c) Atom economy
 - (d) Less hazardous chemical synthesis
3. The solvents commonly used in organic synthesis are
 - (a) Hydrocarbon derivatives
 - (b) Plant products
 - (c) Animal products
 - (d) Renewable feedstocks
4. The alternative feedstock generally used are
 - (a) Plant oils
 - (b) Biomass
 - (c) Plant derivatives
 - (d) All of the above
5. The feedstock used for the traditional synthesis of adipic acid is
 - (a) Glucose
 - (b) Tryptophan
 - (c) Benzene
 - (d) None of the above
6. The feedstock for green synthesis of adipic acid is
 - (a) Glucose
 - (b) Cyclohexene
 - (c) Both of the above
 - (d) None of the above.
7. The solvent not used for green synthesis is
 - (a) Aniline
 - (b) Room temperature ionic liquids
 - (c) Bio solvents
 - (d) Supercritical fluids

8. The feedstock for green synthesis of indigo is
(a) Aniline (b) Glucose
(c) Benzene (d) L-tryptophan
9. Energy consumption can be minimised by the use of
(a) Microwave radiations (b) Ultrasonic radiations
(c) Both of the above (d) None of the above

Solutions

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1 (c) | 2 (b) | 3 (a) | 4 (d) | 5 (c) | 6 (c) |
| 7 (a) | 8 (d) | 9 (c) | | | |

Chapter 23

NANO CHEMISTRY

23.1 Introduction

The introduction of ‘nano’ car by TATA motors has greatly popularised the term ‘nano’ among the Indian masses. The word *nano* signifying very small objects of the range of 1–100 nm has gained importance in the last two decades. *Nano* literally means dwarf (10^{-9}) and can be used as a prefix to the fundamental properties such as mass, time and length to give important scientific properties such as:

Nanogram 10^{-9} g

Nanosecond 10^{-9} s

Nanometer 10^{-9} m.

The science of small objects has grown rapidly in the past two decades as the behavior of matter at ‘nano’ level is considerably different from the bulk behavior of the matter. The physical, chemical, electrical, optical and magnetic properties of nanomaterials are significantly different from the properties of the same material of bigger size. For example, a metal with a grain size of 10 nm is seven times harder and tougher than its counterpart with the size of hundreds of nanometers.

Moreover, the nanomaterials have a relatively larger surface area than ordinary materials and this has a significant effect on their physical properties and chemical reactivities. It has been observed that certain substances that are ordinarily unreactive become reactive in their nanoscale form because of their high surface area. The quantum effects of matter at bulk level and nano level varies significantly. (The specific surface area increases three times when the dimensions decrease from micrometer to nanometer.)

Nanoscience and Nanochemistry It is the science of nanoparticles or the particles whose size varies from 1 to 10 nm in at least one dimension. Nanochemistry exploits this size range for various chemical reactions and chemical purposes, which would not be possible otherwise at the bulk level. Nanotechnology utilizes the behavior of particles at the ‘nano’ level in various production processes.

How much is a nanometer?

One nanometer is equivalent to one billionth (one thousand millionth) of a meter. These particles are not visible to the human eye and can be seen only under a powerful microscope. The size of various objects can help to have a visual perception of a nano-sized objects.

- Human hair is about 100,000 nm wide.
- Red blood cell is about 2000–5000 nm wide.
- Human DNA is 2.5 nm wide.
- Diameter of carbon nanotube is 1.0–1.3 nm.
- Water molecule is about 0.3 nm across.
- An ant is 4 million nm big!

Now you can visualize how small a nanometer is!

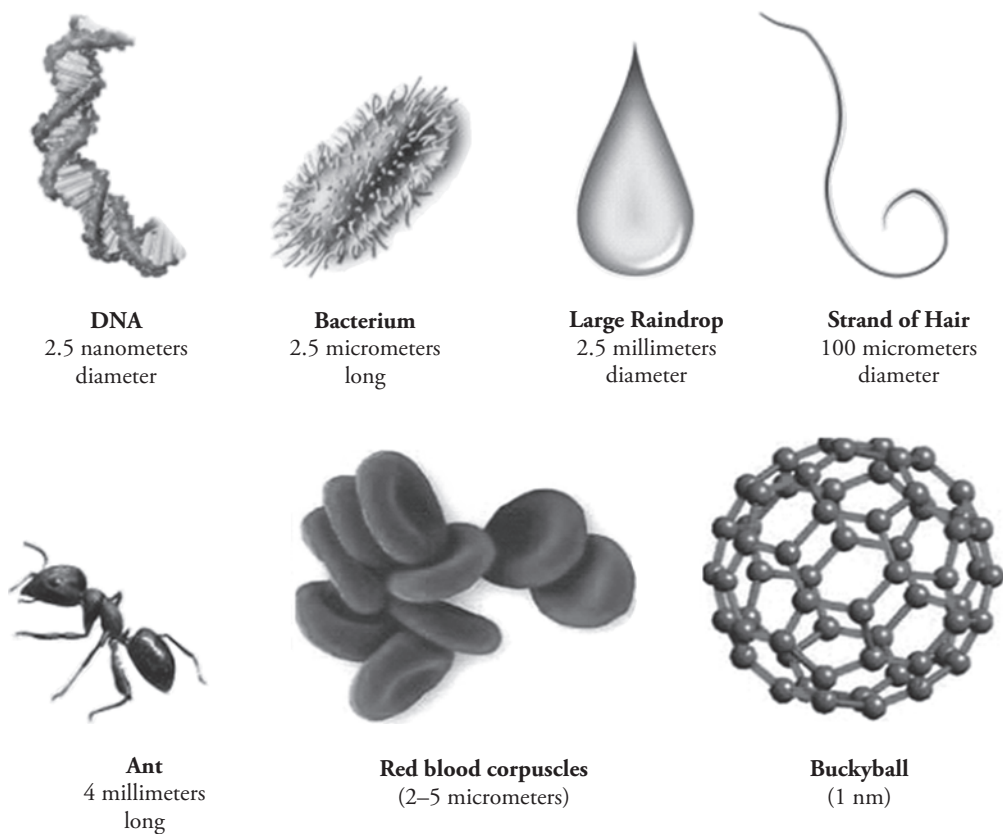


Figure 23.1 *Sizes of various common objects*

23.2 Properties of Nanomaterials

The properties of nanomaterials are very different from those of the bulk material. The nanosize increases the surface area and has a marked effect on the electrical, electronic, optical and catalytic properties. They also introduce many new properties in materials such as bucky tubes (carbon nanotubes) are very stiff and have high tensile strength, and CdSe shows fluorescent emission over a broad range. The properties of materials such as melting point and conductivity show a marked change. Melting point depresses by about 50% in nanoscale and the metals change from conductors to semiconductors and also to insulators. For example, bulk gold is golden in color, it is lustrous, ductile, good conductor of heat and electricity, is chemically inert and does not react with most reagents and is unaffected by air. It has a high melting point of 1080 °C. Nanogold on the other hand is never golden; it has a variety of colors depending upon the shape and size of the nanoparticles. It is not a metal but a semiconductor that melts at a relatively low temperature (~940 °C). Moreover, nanogold acts as a good catalyst. Similarly, the electronic, optical, electrical and catalytic properties of nanosilver are very different from those of bulk silver.

The other effects on the properties of nanomaterials are as follows.

Optical properties

Nanomaterials have interesting optical properties. Optical properties are markedly affected by the shape, size and surface characteristics, doping characteristics and environmental interactions of the nanoparticles. For example, CdSe nanoparticles show fluorescent emission over a broad range.

Electrical properties At nanoscale, the conductivity changes from metal to semiconductors to insulators, that is, from high to low.

Mechanical properties Nanoparticles generally have good tensile strength, elasticity and fracture resistance. They are therefore used as fillers in polymers to improve their mechanical properties.

Magnetic properties Many substances such as gold and platinum which are non-magnetic in bulk become magnetic at the nanosize. Magnetic nanoparticles of Pd, Pt and Au can be obtained from non-magnetic bulk materials.

23.3 Self-assembly

As discussed earlier, nanomaterials are particles having size in the range of 1 to 100 nm at least in one dimension. These materials can be made up of a large number of atoms. Owing to their small sizes, their properties are considerably different from the bulk materials. Nanomaterials can be prepared either by dividing the bulky materials into small particles of the above-mentioned dimension (top-down approach) or by assembling very small particles and binding them to the desired size of 1–100 nm (bottom-up approach). Self-assembly is the basic principle underlying the bottom-up approach that helps to synthesize nanomaterials and enables them to organise into regular patterns with lowest energy configurations. Self-assembly enables very small atoms to be arranged into ordered patterns or arrays to help them perform a particular function. The components assemble or aggregate without the guidance of any external force. For example, alkanethiols form self-assembled

monolayers (SAMS) on gold colloids. CdSe nanoparticles are formed by the self-assembly of atoms into a stable crystalline form (molecular self-assembly). A three-dimensional photonic crystal is formed by the further self-assembly of CdSe nanoparticles (material self-assembly). Other common examples of self-assembly are the formation of surfactants in soap bubbles, crystallisation of water into solid ice, crystallisation of viruses for X-ray determination and alignment of liquid crystals. Biological systems, RNA, proteins and nucleic acids are all self-assembled. Living organisms represent a collection of hierarchically arranged self-assembled structures from molecular to macroscopic level. Nanoscience focuses on self-assembly at a scale of less than 100 nm.

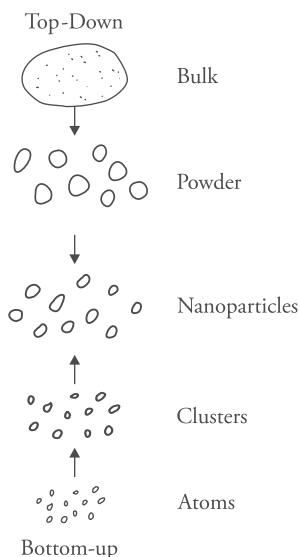


Figure 23.2 The top-down and bottom-up approaches

Principles of self-assembly

1. **Components** The basic units that self-assemble to give patterned structures are the components. These components can be molecules or segments of macromolecules.
2. **Interactions** The driving forces behind self-assembly are weak and non-covalent interactions such as van der Waals forces, electrostatic forces, hydrophobic interactions, π - π interactions, hydrogen bonds and even metal-ligand bonds and coordination bonds. In self-assembly of larger objects of meso- and macro dimensions, other forces such as capillary forces, gravitational attractions, magnetic forces, electromagnetic interactions and entropic interactions also play a significant role.
3. **Adjustability** Ordered structures can be formed by self-assembly only when the components are able to adjust their positions in the aggregate. Hence, it is essential that the forces between aggregates should be weak and easily disrupted by thermal motion. There is equilibria between the aggregated and non-aggregated states.

4. *Environment* The environment greatly affects the patterns of aggregates. By modifying the environment (using boundaries and templates), the self-assembled structures can be tailored as per the requirement.
5. *Mass transport and agitation* Self-assembly occurs only when the molecules are mobile. For small molecules, thermal motion is sufficient to bring the molecules in contact, whereas apart from thermal motion self-assembly of meso- and macro-dimensions require shaking and stirring.

Types of self-assembly

Self-assembly can be static or dynamic. Atomic and molecular crystals, liquid crystals, self-assembled monolayers, colloidal crystals, bubble rafts and liquid bilayers all represent static assemblies. Examples of dynamic self-assemblies are solar system, galaxies, macro- and mesoscopic structures, etc. A few common types of self-assemblies are discussed below

- (i) *Molecular self-assembly* Molecular self-assembly refers to the assembling of molecules without the aid of any external force. The molecules assemble spontaneously into stable and structured aggregates. The driving forces behind molecular self-assembly are reversible non-covalent interactions such as van der Waals forces, hydrogen bonds, metal–ligand bonds, π – π interactions, etc. The reversibility of forces help components of self-assembled aggregates to adjust mutually. Molecular self-assembly can be intermolecular as well as intramolecular. Intramolecular self-assembly generally brings about folding and the term molecular self-assembly actually refers to intramolecular self-assembly.
- (ii) *Material self-assembly* Material self-assembly results from the assembling of various nano-sized blocks. In these lattices, the atoms of conventional solids are replaced by nanomaterials. In material self-assembly, the organic, inorganic and polymeric chemical components with well-defined functions integrate into electronic, photonic, mechanical, analytical and chemical systems for an intended nanotechnological application. Systems capable of performing electronic operations such as switching, gating, rectification and amplification are designed by using materials' self-assembly.

Molecular v/s material self-assembly

In molecular self-assembly, the molecules enter into self-organisation, forming structures with properties different from the individual constituent moieties.

In material self-assembly, the individual blocks make up a useful and thermodynamically stable structure.

Self-assembling materials

- (a) **Ultrathin film** It is a 1-Å-thick film of atom spread on a flat surface. The film is produced by the vaporisation and subsequent deposition of atoms on a solid substrate. This technique that produces one-atom-thick layers is called the atomic layer deposition. Ultrathin films are not very stable and the surface atoms get clustered to form a thick film several atomic layers in thickness.

- (b) **Langmuir–Blodgett (LB) film** A dilute solution of amphiphilic molecules (molecules having both water-loving and water-hating parts) spread on the surface of water. These molecules do not dissolve in water and when the solvent sticking to them evaporates they are left floating at the water–air interface and organise into a one-molecule-thick layer (monolayer), two-molecule-thick layer (bilayer) or several-molecule-thick layer (multilayer) (Fig. 23.3).

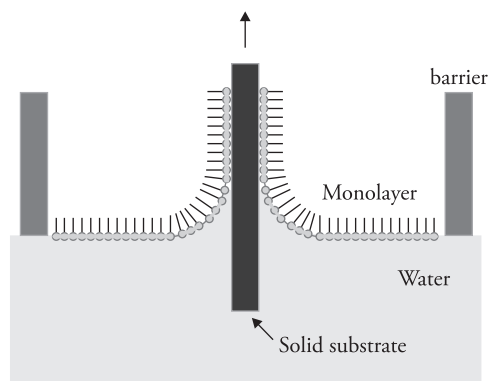


Figure 23.3 *Langmuir–Blodgett film*

The polar part of the molecule attaches itself to water and the non-polar hydrophobic region orients away from the surface. The hydrophobic region of neighboring molecules stick to each other. The surface area is then decreased by compressing the monolayer with a moving barrier while monitoring the surface pressure. This results in the formation of a two-dimensional condensed monomolecular layer at the water–air interface. Such layers are formed by surfactants above the critical micellar concentration.

- (c) **Self-assembled monolayer** A self-assembled monolayer (SAM) is formed by the adsorption of an active surfactant on a solid surface. An SAM film can be deposited by vapor phase deposition. The formation of SAMs does not require the application of external pressure.

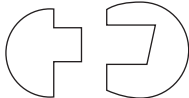
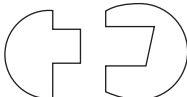
Self-assembly helps in the formation of monolayers of organic molecules on noble metals. Monolayers made of long-chain organic molecules with functional groups such as -SH, -CN, -COOH and -NH₂ are deposited on metal surfaces such as Au, Cu, Ag, Pd, Pt and Hg as well as semiconducting surfaces such as Si, GaAs, Indium coated tin oxide (ITO), etc. SAMs find application in the manufacture of monoelectronic devices, sensor arrays, super capacitors, catalysts, rechargeable power sources, etc.

Monolayers on gold Self-assembled monolayers of organic molecules such as thiols or phosphonic acids are deposited on gold surface. The thiol molecules get covalently bonded to gold surface and get arranged in two dimensions over the gold surface. These layers are stable because of bond formation between the gold surface and the organic molecules.

- (d) **Mesoscale self-assembly (MESA)** The size of mesoscale self-assembly (MESA) varies from 10 nm to 10 mm (1cm). The components of MESA are bigger than molecules; hence, apart from the forces employed in molecular self-assembly they can utilise a wide range of other interactions such as capillary, electrostatic, magnetic, optical, gravitational and fluidic

sheer. The self-assembly of objects in a mesoscale can be used to fabricate complex systems that cannot be made otherwise. Mesoscale objects self-assemble to yield colloidal crystals, bubble raft, two-dimensional arrays of nanometer- and micrometer-sized beads, gold colloids assembled by DNA duplex formation, etc.

Table 23.1 Comparison of molecular and mesoscale self-assembly

S.N	Molecular self-assembly	Mesoscale self-assembly
1	The size of molecules is small in the range of few nanometer.	Component size is bigger in mesoscale self-assembly and varies from 10 nm to 10 mm (1 cm).
2	Reversible non-covalent interactions such as van der Waals forces, hydrogen bonds, metal–ligand bonds, $\pi - \pi$ interactions guide the self-assembly. Electrical and magnetic interactions do not support molecular self-assembly.	Apart from the forces of molecular self-assembly, the additional forces responsible for mesoscale self-assembly are capillary, magnetic, optical, fluidic shear, electrical and gravitational.
3	The components of molecular self-assembly are molecules and the properties of individual molecules and the self-assembled structure vary significantly.	In MESA, the individual component makes the final structure. The function desired in the final structure must exist in the component.
4	The components of self-assembled structures move and interact to form assemblies. In molecular self-assembly, thermal motion is sufficient to bring the molecules in contact.	As the components are larger in size, apart from thermal motion, molecular contact in MESA it requires motion by external sources such as shaking or stirring.
5	<p>The components assemble by balancing both attractive and repulsive forces. Complementary shape of interacting components assists self-assembly.</p>  <p><i>Complementary shape to assist self-assembly</i></p>	<p>As the components assemble by balancing both attractive and repulsive forces. Complementary shape of interacting components assists self-assembly.</p>  <p><i>Complementary shape to assist self-assembly</i></p>
6	Templating or use of guides to control self-assembly is not possible for molecular system.	Owing to their bigger size the self-assembly can easily be guided using templates that can be in the form of containers of appropriate size.

Construction of MESA

- (i) **By capillary interactions** These are used for the self-assembly of micrometer- to millimeter-sized components into electronic devices and other structures with electrical conductivity. Capillary interactions are generally used as the forces driving the self-assembly. It helps to minimise the interfacial forces (surface tension) and finds its use in fabricating optically active materials such as 3D microelectromechanical systems (MEMS) and microoptoelectromechanical (MOEMS) devices. Similarly, hydrophobic and hydrophilic sets are selectively patterned to form a 2D aggregate. While floating at the interface between a hydrophobic liquid (say perfluorodecalin, PFD) and a hydrophilic liquid (say water), these

objects self-assemble. The capillary forces resulting from the presence of a liquid polymer help in assembling the structures in one or multiple layers.

- (ii) **Self-assembly by spontaneous folding** This strategy finds application for the formation of 3D objects. The flat, elastomeric sheets patterned with magnetic dipoles fold spontaneously to form 3D structures.
- (iii) **Hierarchical self-assembly** The components are arranged in a hierarchical manner into increasingly complex structures. This is commonly found in biological systems. Patterned 3D structures can be obtained by hierarchical self-assembly, for example, beads assembled into rods in columnar wells. These rods then self-assemble to form 3D arrays.
- (iv) **Templated self-assembly** The 3D structures and their alignment patterns can be controlled using templates. For the formation of spherical aggregates of colloids or self-assembly of hexagonal rings, a liquid drop can be used as a template. For this, hexagonal rings are prepared and suspended in a continuous phase. When a drop of a discontinuous phase is added, there is spontaneous development of a spherical liquid–liquid interface. The hexagons segregate and are ordered on this interface.
- (v) **By changing solvent polarity** CdSe nanocrystals assemble into a 3D array by changing the polarity of the solvent.
- (vi) **By adsorption** Nanocrystals adsorbed on polymers and biomolecules spontaneously assemble into high-order superstructures forming mesoscale self-assembly.
- (vii) **Dynamic self-assembly** They are formed with the help of magnetic forces produced by a rotating permanent magnet. Millimeter-sized magnetic disc spinning at the liquid–air interface when placed in this magnetic field produces dynamic patterns with regularity of very high order.

Applications

- Technologies based on MESA find application in the field of microelectronics, microelectromechanical systems (MEMS), chemical and biosensors and microanalytical devices.
- Self-assembly can be used to control properties of the newly constructed materials. They find applications in light-emitting diodes (LEDs), switching devices, optical memories, molecular fillers and optical waveguides.
- Photonic crystals allow us to trap light and control the way it propagates. They self-assemble to form ‘smart plastics’ that find potential applications in the field of optical data storage and telecommunications.
- Self-assembled materials find use in creating optoelectronic array and three-dimensional arrays for holographic data storage.
- Molecular self-assemblies help in creating a new class of magnetic materials which can be used in computer as hard discs and allow 100 times more data storage than the present conventional products.
- Self-assembled nanocomposites can be used for developing devices such as nano-batteries where the anode, cathode and electrolytes are organised into an appropriate nanostructure.

23.4 Preparation of Nanomaterials

Nanomaterials can be synthesised in a number of ways. The various methods generally employed for the synthesis of nanomaterials are as follows.

- (i) **Mechanical grinding** This method of synthesis of nanomaterials follows a top-down approach. In this method, the nanoparticles are not synthesised by assembling small particles but by the structural decomposition of larger particles by the use of mechanical mills. This method is simple and inexpensive but causes environmental pollution.
- (ii) **Wet chemical synthesis** Wet synthesis can follow the top-down approach in which a single crystal is etched into nano-sized particles in aqueous solution. Porous silicon is synthesised by electrochemical etching. It can also follow a bottom-up approach where small particles agglomerate in a controlled manner to form nanosized particles.
 - (a) *Sol gel process* It is a very popular method used for the preparation of oxide nanomaterials. The sol–gel process involves hydrolysis followed by condensation. A metal or metalloid employed as a precursor is dispersed in acid or water to form a sol. Gel is obtained from this sol by the removal of water.



Metal alkoxide



The various steps involved are as follows:

- (i) First the solvated solution of the alkoxide or metal is formed.
- (ii) Solvation is followed by polycondensation due to the formation of oxide or alcohol-bridged network. This leads to gelation and increases the viscosity of the solution dramatically.
- (iii) Gradually, the gel solidifies and the smaller particles aggregate to form larger particles, a process called coarsening.
- (iv) This is followed by drying of the gel where water and volatile liquids are removed from the gel network. After this the surface-bound M-OH groups are removed so that the gel is stabilised against rehydration.

The above method of synthesis follows the bottom-up approach, where it is essential to control the growth of the agglomerating particles. The bottom-up method, although slow, leads to the formation of mono-sized nanoparticles.

- (2) **Gas-phase synthesis of nanomaterials** Gas-phase synthesis is gaining importance as they have certain advantages

Advantages

- The size, shape and chemical composition of the nanomaterials can easily be controlled.
- Substances formed are of high purity.
- The reaction mechanism is easily controllable.

The conventional gas phase synthesis is the chemical vapor deposition (CVD) method that can be either homogeneous CVD or heterogeneous CVD. In these synthetic routes, small clusters of nanoparticles are produced because of condensation.

In homogeneous CVD, the particles in the gaseous phase diffuse under the influence of thermophoretic forces and deposit on the cold surface. These deposits are either scrapped off to yield nanopowders or 'particulate films' are formed by depositing them onto the substrate.

Chemical vapor deposition can be achieved in a number of ways

- (a) **Furnace heating** The appropriate material is heated in a furnace upto a temperature of 2000 °C. The material is evaporated in an inert atmosphere (e.g., helium). If a compound is to be formed then the precursor is fed at very low pressure into the furnace in the presence of the substance with which it has to react. The hot particles are then condensed into small clusters. The clusters grow as long as they are in the supersaturated region. The size is controlled by removing them rapidly from the supersaturated region with the help of a carrier gas. This method is simple and the particle size can be controlled by controlling the rate of evaporation, rate of condensation and the rate of removal of cluster with the assistance of carrier gas.
- (b) **Flame-assisted ultrasonic spray pyrolysis** In this method the precursor is nebulised to obtain its vapors. These vapors are then pyrolysed by burning in an acetylene oxygen flame or hydrogen oxygen flame. The high pressure may result in highly agglomerated powders; hence, the low-pressure range is maintained to reduce the aggregation of particles. This method is used to obtain ZrO_2 nanoparticles [precursor $\text{Zr}(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_4$] and silica nanoparticles (silica tetrachloride is heated in an oxyhydrogen flame). It is also widely used to obtain titanium dioxide, fused silica and carbon black. As the flame has an oxidative atmosphere, this method is limited to the formation of oxides (Fig. 23.4).

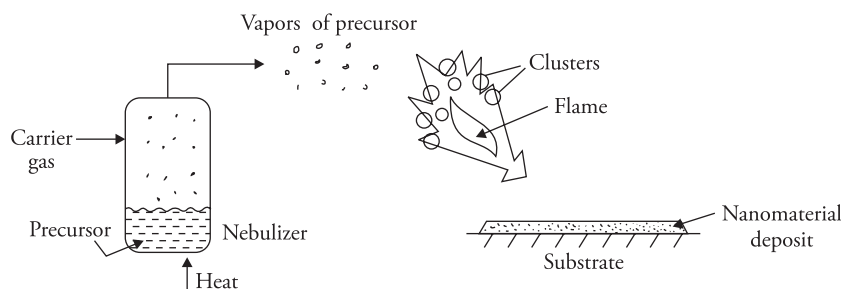


Figure 23.4 Flame assisted ultrasonic spray pyrolysis

- (c) **Gas condensation processing (GPC)** In this method the desired substance is vaporised by thermal evaporation or by sputtering in an inert atmosphere of He, Ne, Ar and Kr or by a laser beam. The particles are then condensed and collected either in a solvent or by deposition on a collection device. This method helps in the synthesis of pure nanocrystalline substances. Generally, refractory metal crucibles of W, Ta or Mo are used for evaporation, and if the substance reacts with crucible then evaporation is accomplished by a laser beam or electron beam.

- (d) **Chemical vapor condensation (CVC)** In chemical vapor condensation, the source of evaporation is replaced by a hot wall reactor. To avoid the formation of thin films and to promote homogeneous nucleation of precursor particles the gas flow rate and residence time of the precursor particles is adjusted.

The vapors of precursor are introduced into the hot wall reactor, where, by adjusting the conditions, nano-sized clusters are formed that are condensed and removed. This method is useful for the synthesis of nanoparticles of nitrides, carbides, BaTiO_3 or other composite structures (Fig. 23.5).

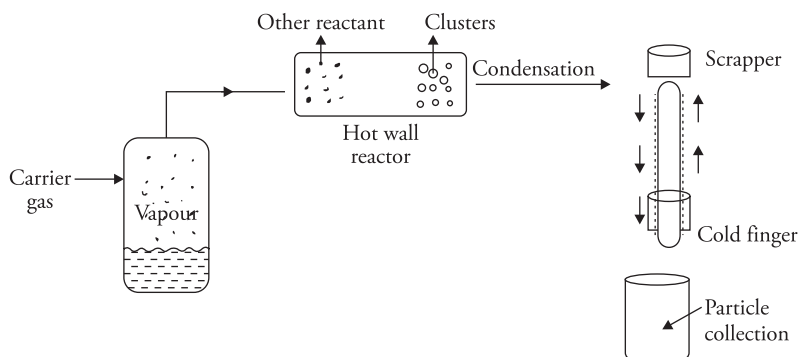


Figure 23.5 Schematic representation of a CVC reactor

- (e) **Sputtered plasma processing** This method is similar to the gas phase condensation method, except that the precursor is sputtered using rare gases and then the particles agglomerate to produce nanomaterials. This method finds use in the synthesis of nanoparticles of various alloys, oxides, carbides, nitrides, etc.
- (f) **Microwave plasma processing** In this technique the precursor is vaporised using plasma instead of high temperature. In this method, the precursor is introduced from the front of the reaction vessel that is made of quartz and is placed in a cavity connected to a microwave generator. The advantage of plasma-assisted pyrolysis is that the precursor can be activated at low temperatures that prevent the excessive agglomeration of the primary particles. The primary precursor can be coated with another phase by introducing the second precursor into the reactor. This method is employed for coating ZrO_2 nanoparticles with Al_2O_3 . The inner ZrO_2 is crystalline, whereas Al_2O_3 is amorphous. By reversing the reaction sequence amorphous Al_2O_3 can be coated with crystalline ZrO_2 . This method can be used to obtain both nanoparticles as well as thin film of nanoparticles.

23.5 Nanomaterials

Nanomaterials form the basis of nanoscience and nanotechnology. They are very small materials with the particle size ranging from 1 to 100 nm. The different types of nanomaterials are as follows

1. Carbon nanotubes

Carbon nanotubes are considered as allotropes of carbon belonging to the fullerene family. A carbon nanotube consists of a sheet of carbon atoms that are sp^2 -hybridised and have a hexagonal symmetry. Such a two-dimensional sheet is called graphene. A carbon nanotube is produced by rolling a graphene sheet into a cylindrical shape.

The tube can be opened or closed at the ends by half fullerene. The length is several times the width and the ratio of length to diameter is of the order of 100; hence, carbon nanotubes are considered as 1D structure. The properties of CNT depend in the manner in which the graphene sheet is rolled.

- They have unique electronic and mechanical properties.
- They are 100,000 times thinner than the human hair.
- They combine rigidly and flexibly and can be hundreds of times stronger than steel, but six times lighter.
- They possess very high tensile strength and stiffness.
- Their compression strength is in the range of 100–150 GPa.
- They can withstand large strains and show considerable elasticity and capability of atomic rearrangement.
- Their electronic properties depend on the manner in which they are closed at the ends. The electronic properties are greatly influenced by the symmetry and helicity or chirality with respect to the tube axis. This alignment, however, does not affect the mechanical properties of CNTs.
- They possess high conductivity, chemical specificity and inertness.

Types of carbon nanotubes

There are two types of CNTs:

- Single-walled (one tube) SWNT
- Multi-walled (several concentric tubes) MWNT

Individual nanotubes align themselves through non-bonding interactions such as van der Waals forces, pi stacking to form ropes.

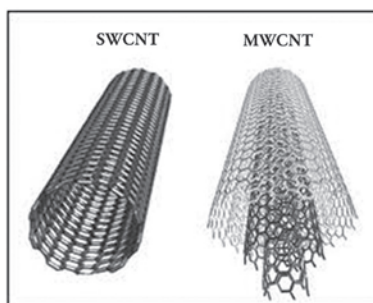


Figure 23.6 Carbon nanotubes

Source: Veena Choudary and Anju Gupta (2011). Polymer/Carbon Nanotube Nanocomposites, Carbon Nanotubes – Polymer Nanocomposites, Dr. Siva Yellampalli (Ed.) ISBN: 978-953-307-498-6, InTech, DOI:10.5772/18423. Available from: <http://www.intechopen.com/books/carbon-nanotubes-polymer-nanocomposites/polymer-carbon-nanotube-nanocomposites>

Synthesis

Carbon nanotubes are produced in the following manners:

- (i) Evaporating graphite rods in a dynamic atmosphere of helium.
- (ii) Laser evaporation of graphite produced SWNT. A mixture of graphite is heated with Fe and Ni catalysts at 1200 °C and the material is irradiated with laser. It yields 50%–70% CNT.
- (iii) SWNTs and MWNTs can be synthesised by chemical vapor deposition. An organometallic precursor and carbon-containing feed gas are mixed and pyrolysed in a quartz tube. The nanotubes thus formed are collected from the cooler end.
- (iv) Both MWNTs and SWNTs are formed with carbonaceous matter and can be separated by heat treatment. The amorphous carbon material is burnt off by heating the soot at 750 °C for half an hour; the product thus obtained is a mixture of nanotubes.

Applications

CNTs have a wide range of potential applications because of their exceptional material properties such as high electrical and thermal conductivity, strength, stiffness and toughness. They find their use in the manufacture of reinforced composites, sensors, nanoelectronics and display devices. Some of their applications are as follows:

- (i) SWCNT is strong and stiff with strength hundreds of times stronger than steel and are much lighter; hence, they are used for making light but strong composite materials. SWNTs are the strongest known material. Owing to their strength, they are widely used in manufacturing reinforced plastics, car and aeroplane parts and in sports goods.
- (ii) MWCNTs have good heat and electrical conductivity and they find use in chemical sensors, conducting paints, hydrogen storage and in the manufacture of composite materials.
- (iii) SWNTs find use in solar panels because of their tendency to absorb ultraviolet/visible and near infrared light.
- (iv) SWNTs are used for hydrogen storage owing to their capillary effects.
- (v) Electrically conducting CNT films are used in LCDs, touch screens and photovoltaic devices. These films are also used for displays in computers, cell phones, ATMs, etc.
- (vi) MWNTs generate strong electrical field and are used for electric motor brushes.
- (vii) MWNTs are used in lithium ion batteries and silicon-coated carbon nanotubes are used as anodes for Li- ion batteries.

- (viii) In medical fields, CNTs are used in implant materials and nanotubes loaded with drugs can be applied directly to the affected area.
- (ix) CNTs are used for the treatment of cancer. They absorb light from infrared laser and incinerate the tumor.
- (x) CNTs find use in water purification.
- (xi) They are used in stain-resistant textiles.

2. Nanocrystal

A nanocrystal is an inorganic entity in which the constituent atoms or ions have a crystalline arrangement in at least one dimension and their size is less than 100 nm. Semiconductor nanocrystals with size <10 nm are termed as 'quantum dots'.

Nanocrystals can be synthesised from vapor phase by crystallisation on substrate through heterogeneous nucleation or by controlled homogeneous nucleation in a super-saturated liquid phase. The agglomeration of the nanocrystal is prevented by capping them with suitable capping or protecting agents. For example, nanocrystalline gold is prepared by the reduction of gold ions in solution of citrate ions. The agglomeration of the colloidal sol is prevented with electrostatic repulsion between the Au particles that are covered by negatively charged citrate ions. The size of gold ions can also be controlled by 'capping' them with thiol molecules.

The nanocrystals link molecules and bulk materials. Their properties depend strongly on their dimension and change continuously as a function of their size. For example, the color, sharpness and magnetic properties of semiconductor-based nanocrystal devices varies with the size of the nanoparticles.

Applications

Nanocrystals have a wide variety of applications, some of which are as follows:

- In dye-sensitised solar cells.
- In medical imaging and as biotags for the identification of genes.
- In the analysis of proteins and in the manufacture of drugs.
- In electronic industry, they find use in flat-panel displays, magneto-optical memory chips, in optical and infrared laser, etc.
- Zeolite nanoparticles are used to filter crude oil and separate diesel from it.

Quantum dots

Quantum dots are nanoparticles that range from 2 to 10 nm in diameter and are made strictly from semiconductor materials such as chalcogenides (selenides and sulfides) of metals such as cadmium or zinc (CdSe or ZnS). They can be prepared both by the top-down approach and the bottom-up approach. The top-down approach includes milling and grinding, whereas in the bottom-up approach one can use gas phase or liquid state approaches (for details, refer to Section 23.4). The size and structure of the quantum dots can be carefully controlled. All the general methods used for

the preparation of nanomaterials can be applied to the synthesis of quantum dots. The InP (indium group III and phosphorus group V) quantum dot can be synthesised as follows.

Indium oxalate, indium chloride or indium fluoride are used as precursors for indium, and trimethylsilylphosphine is used as the precursor for phosphorus. A mixture of trioctylphosphine oxide (TOPO) and trioctylphosphine acts as colloidal stabilisers. The precursors are decomposed at a temperature greater than 200 °C. The nanocrystals are precipitated by adding methanol to the dispersion.

Properties

The optical properties of quantum dots are affected by the nature and area of the surface. Their properties change significantly when an electron leaves the surface. Quantum dots emit photons under excitation and these are visible to the human eye as light. By controlling their size, it is possible to monitor their wavelength of emission and this in turn determines the color of light perceived by the human eye.

Applications

Quantum dots find diverse applications in varied fields:

- They are used in photolysis reactions and in the manufacture of dye-synthesised solar cells (for details, refer to Section 18.10).
- Similar to nanocrystals, quantum dots also find their application as biological labels, bioconjugates and as drug carriers.
- In the electronic industry, they are used for the preparation of photovoltaic cells and other electrochromic devices.
- They also find use in environmental technologies for the removal of pollutants from the environment (CdS nanocrystals fix atmospheric carbondioxide).

Nanowire

Nanowires have diameter of the order of a nanometre (10^{-9} m) and their length-to-width ratio is greater than 1000; hence, they are also referred to as a one-dimensional material. They can be of various types:

- Metallic (e.g., Ni, Pt and Au).
- Semiconducting (e.g., silicon, gallium nitride and indium phosphide).
- Insulating (e.g., SiO_2 and TiO_2).
- Molecules that have repeating molecular units. They can be organic (DNA) or inorganic ($\text{Mo}_6\text{S}_{9-x}\text{I}_x$).

Properties

Depending upon the material with which the nanowires are made, they can be metallic, semiconductors or insulators. Nanowires behave like ballistic conductors. In normal conductors, the speed of the conducting electrons reduces because of collision with atoms, whereas in ballistic

conductors electrons travel through the conductor without colliding with the atoms. Nanowires can conduct efficiently without heating the conductor wire.

Applications

Nanowires find extensive applications because of their remarkable optical, electronic and magnetic properties. They find uses in

- (i) Nanowires conduct electricity; hence, they are used in making miniature circuits for transistors and other basic electronic devices such as junction diodes and logic gates.
- (ii) Nanowires are also used in quantum computers. Research has shown that indium arsenide nanowires when attached to aluminium electrode make aluminium a superconductor at low temperature because of proximity effect.
- (iii) Nanowires can also generate electricity from kinetic energy (piezoelectric effect). Piezoelectric nanowires can be used in future to provide power to nano-sized systems. Coaxial nanowires improve the efficiency of solar cells.
- (iv) Nano-sized devices such as nano robots are made of nanowires; these nano robots are used to treat diseases such as cancer.
- (v) Used in thermoelectric cooling systems.
- (vi) Nanowires are used to link tiny components in extremely small circuits.

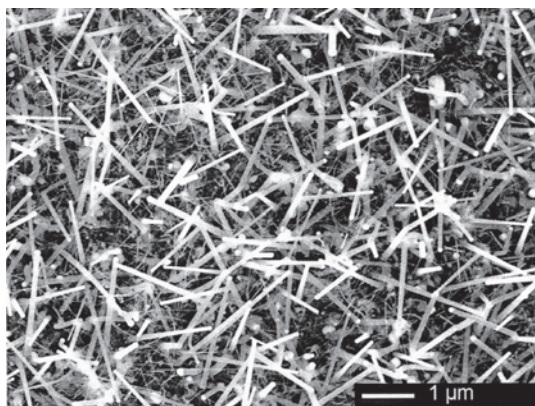


Figure 23.7 Germanium nanowires

Source: <https://www.intechopen.com/books/nanowires-fundamental-research/growth-of-germanium-nanowires-on-a-flexible-organic-substrate>

Carbon nanocones (nanohorns) They are conical structures made of carbon with one nanometer diameter at least in one dimension. Unlike nanowires, the height and base diameter in nanocones is the same. The single-walled carbon nanohorns (SWNH) form one class of such conical structure with a sharp apical angle.

Carbon nanocones are produced by the pyrolysis of heavy oil with a plasma torch having temperature above 2000 °C.

Nanocones can also be prepared by heating the graphite surface with an intense short laser pulse so that some carbon from the graphene sheet evaporates and other atoms rearrange to form a conical structure.

Nanowires find use in the photovoltaic industry. Research has proved that hybrid solar cells covered with silicon nanocones improve their performance tremendously. Nanocones, because of their shape, enhance the absorption of light and reduce scattering and reflection of light. This helps in the production of economically viable photovoltaic devices. Nanocones are also used as capsules for drug delivery. They are cheaper and more easily produced than carbon nanotubes.

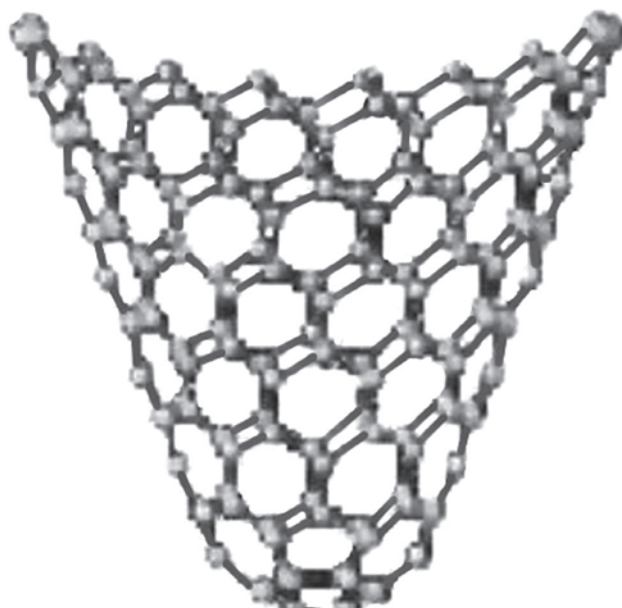


Figure 23.8 • *A carbon nanocone*

Source: http://commons.wikimedia.org/wiki/File:Carbon_cone_tip.JPG

Haeckalites Haeckalites, named in the honour of the nineteenth century German zoologist Ernst Haeckel, consist of a layered structure of pentagons, hexagons and heptagons. They can also be rolled like carbon nanotubes to give tubular structures. In the rolled structures, the bands of heptagons have a negative curvature and bands of pentagons have a positive curvature. The haeckalite nanotubes may have different structures such as nanocoils, string of pearls, corrugated cylinders, etc.

The stiffness and Young's modulus of haeckalites is of the same order of classical carbon nanotubes.

Haeckalites find application in lithium storage, hydrogen storage, electronic devices, in the medical field, manufacture of sensors, etc.

23.6 Surface Characterisation Techniques

Nanoparticles have vast medical, environmental and engineering applications. The properties of nanoparticles are dependent on size and structure hence it is important to understand the structure of nanoparticles as it enables us to correlate the physicochemical properties of nanomaterials with their chemical, ecological or biological responses. Characterisation of nanomaterials helps in understanding the physical and chemical properties of nanomaterials. It also helps in determining the structure at atomic and microscopic levels. Bulk properties like shape, size, phase, electronic structure and crystallinity and surface properties like arrangement of surface atoms, surface area, surface composition and surface electronic structure are determined by the various characterisation techniques.

To study the structure of nanomaterials they are observed using electrons, photons, scanning probes, ions, atoms, etc. The commonly used techniques are Brunauer–Emmet–Teller (BET) surface area analysis, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), inductively coupled plasma atomic emission spectroscopy (ICP-AES), ultraviolet–visible spectroscopy, nuclear magnetic resonance spectroscopy (NMR), etc. A brief description of BET surface area analysis and TEM is given below.

1. *BET surface area analysis*: This method helps in determining the surface area, pore size and pore size distribution of nanomaterials. This is done by gas sorption method. Prior to determination the adsorbed foreign particles are removed from the surface of the adsorbent by heating and degassing by vacuum force. Sometimes instead of subjecting the adsorbent to vacuum force it is cleaned by flushing the adsorbent with an inert gas at elevated temperature. After cleaning the sample is brought to a constant and very low temperature usually in a dewar flask containing liquid nitrogen (77.4 K). Controlled doses of adsorbate gases are admitted into the evacuated sample chamber. They are first adsorbed and then desorbed. Adsorption and desorption isotherms are obtained by subjecting the gas to a wide range of pressures. The amount of gas adsorbed or desorbed is estimated by noting the pressure variations due to adsorption or desorption of the adsorbate gas molecules on the adsorbent. By knowing the area occupied by one adsorbate molecule the total surface area can be determined using the adsorption model. Similarly the pore size and the pore size distribution of porous materials can be found from the adsorption/desorption isotherm using an assessment model.
2. *TEM*: This technique is used for the structural informations of solid material both by imaging and by electron diffraction. In TEM, a thin specimen is irradiated with an electron beam of uniform current density; the electron density is in the range of 60–150 (usually 100 keV). For high-resolution TEM (HRTEM) or high voltage electron microscope HVEM the electron density of 200 keV–1 MeV is used. The electrons emitted from the electron gun by thermoionic emission from tungsten cathodes or LaB₆ rods enter the sample and are scattered as they pass through it. They are then focused by the objective lens and amplified by the magnifying projector to produce the desired image (Fig. 23.9).

The incident electron beam interacts strongly with the atoms leading to scattering which can be either elastic or inelastic. Elastic scattering is highly localised, involves no energy loss and gives rise to a diffraction patterns whereas inelastic scattering is more diffuse and spreads over about a nanometer. Inelastic scattering generally occurs at heterogeneities like grain boundaries, defects, dislocations and areas of density variations. It causes complex absorption and scattering effects leading to the spatial variation in the intensity of the transmitted electrons.

Greater spatial resolution can be achieved by high voltage TEM instruments (e.g., with 400 kV). High-voltage instruments provide better resolution; they have greater electron penetration because high-energy electrons interact less strongly with matter than the low energy electrons. High voltage instruments enable us to work with thicker samples. TEM provides information about the particle size, morphology and also provides an insight into the particle aggregation.

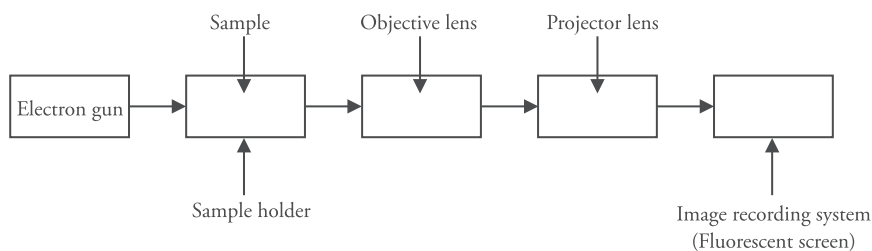


Figure 23.9 Outline sketch of TEM

23.7 Applications of Nanomaterials

1. **Medicine** Nanoparticles are being used for the diagnosis and treatment of various diseases. Nanomaterials are used in medicine as drug carriers. Their large surface area enables them to load the drug on them and their small size helps them to transport these drugs into the cells, nuclei and across the membranes. In 1959, Nobel laureate Richard Feynman in his famous talk on 'Plenty of room at the bottom' suggested the concept of effective use of nanotechnology in disease treatment.

The nanoparticles can be coated on the drug (nanospheres), filled in a cavity surrounded by a polymeric layer (nanocapsules), the drug can be contained in holes inside nanoparticles (nanopores) or in branched-tree-shaped nanoparticles (dendrimers).

Biodegradable nanoparticles are used to carry antibiotics to specific sites. Nanotechnology also has widespread diagnostic applications. It is used in early diagnosis of various forms of cancer.

2. **Catalysis** The nanoparticles have large surface area and hence provide higher catalytic activity. This property finds use in catalysis by precious metals such as Pd, Pt and Rh. These metals are widely used as catalysts but they are very expensive. The nanosize of these catalysts increases the reactive surface area, making them extremely active and thereby economising

their use. The active metal nanoparticles are supported on powdered material in the form of beads, platelets, etc.

Similarly, although bulk aluminium is used for making utensils, nanoaluminium becomes so reactive that it finds its use as a solid fuel in rocket propulsion. It supplies the required thrust to propel the rocket in space.

3. **Environmental technologies** Nanoparticles are being widely used to control environmental pollution. Nanoparticles on powder supports or on tubular monoliths form a catalytic system used widely in the removal of pollutants such as oxidation of volatile organic compounds (VOCs) in chimneys. Oxidation of flue gases in the catalytic converters of petrol-burning internal combustion engines where CO is oxidised to CO₂ (in the presence of Pt catalyst). NO_x is removed by reducing it to N₂ in the presence of CO (catalyst Rh), and hydrocarbons are oxidised to CO₂ and H₂O using Pd catalyst.

Similarly, cerium oxide nanoparticles are used in diesel engines for pollution control. They trap the carbon particles (soot) formed because of incomplete combustion, hence are used in filters.

4. **Electronics and related fields** Nanomaterials are widely used in electronic circuits used in television, radio, telephone, automobiles, aeronautics, etc. Use of nanomaterials helps in reducing the size of these gadgets.

The properties of particles of nanodimensions are used to develop sensors whose functional units are nanoentities, although the material itself is not nano in dimension. The high surface-to-volume ratio of nanomaterials, their optical, electrical and physical properties help them initiate response to the minute change in the concentration of the species to be detected. Solid-state techniques can also be used to create devices known as nanoelectromechanical system or NEMS that are related to microelectromechanical system or MEMS.

- *Batteries* Nickel metal hydride batteries made of nanocrystalline nickel and nickel hydrides last longer and require less frequent charging.
5. **Mechanics** Nanoparticles are used to improve the performance of tyres and improve mechanical properties of ceramics and alloys. The common uses of nanoparticles to improve the mechanical properties are as follows:
 - *Tyre* The properties of a good tyre include reduced roll resistance that decreases the petrol consumption, good road holding capacity especially when the road is wet or covered with snow and it should have resistance to wear to improve its lifetime. Nanoparticles of precipitated silica are added to tyres to improve their resistance to rupture, increase hardness and make them more durable. These highly dispersible silica (HDS) improve their road holding capacity, reduce roll resistance and increase their resistance to wear.
 - Addition of nano-structured particles to metal–ceramic composites (cermets) improve their hardness, tensile strength and elastic modulus-bonding strength.

- Alumina nanofibers and carbon nanotubes added to polymers make them stiffer, prevent them from deformation, increase stability to heating effects, make them more water-resistant and improve their load-bearing strength.
 - Polymers such as polylactic acid (PLA) are used for packing food and medicines, although biodegradable they lack mechanical strength. Addition of clay improves mechanical strength without affecting its biodegradability.
 - Nanoporous solids act as shock absorbers and molecular springs. This is accomplished by intruding a lyophobic liquid (non-wetting liquid) inside the porous solid. They find application in car bumpers, suspension for vehicles, devising systems to protect buildings from seismic vibrations and various other devices. The lyophobic liquid is intruded and extruded on the application and release of pressure.
6. **Surface nanoengineering** Nanoparticles are used for making self-cleaning surfaces. Water from the damp air condenses on the glass surface, making it difficult to see through it. Coating these glass surfaces with TiO_2 nanoparticles make the glass hydrophilic, rather than hydrophobic so that the condensed droplets spread as a continuous layer and prevent the distortion of visual image. Similarly, deposition of TiO_2 nanoparticles on ceramic and polymer surfaces leads to self-cleaning surfaces.
7. **Miscellaneous uses**
- Nano titanium oxides are used in cosmetics to prevent the skin from solar radiations (preparation of sun screens).
 - The luminescent materials that glow when struck by a beam of electrons are called 'phosphors'. These phosphors are widely used in television screens, for detection of forgery in bank notes, scintillators in medical fields, etc. The reduction in size improves the resolution of monitors. Nano phosphors are also used as fillers in cosmetics, varnishes and technical fibers. Owing to the nanoparticle size of the fillers the visible wavelengths do not interact and light passes easily, thereby maintaining the transparency.
 - In the medical field, these phosphors are fixed on proteins and can easily pass through the cells and membranes helping in the diagnosis and cure of diseases.
 - In environment studies, nanophosphors act as non-polluting and non-radioactive markers and help in the detection of the flow of liquid or gas leakage, etc.
 - **Food packing** Nanosensors find use in food packaging as they are capable of changing color when the food is no longer edible.
 - **Lubricants** Nanospheres are widely used for lubrication.
 - **Magnetic materials** Magnets made of nanocrystalline yttrium–samarium–cobalt grains possess exceptional magnetic properties because of their larger grain interface area. These magnets find use in motors, in medical field, in magnetic resonance imaging (MRI) and in microsensors.

Nanoscale magnetic materials are used for data storage devices such as computer hard discs. The use of nanoparticles improves the storage capacity of the disc.

Summary

- Nanoscience is the science of small objects ranging from 1 to 100 nm size at least in one dimension.
- Nanochemistry utilises the nano-sized particles for various chemical reactions.
- The electrical, electronic, optical and catalytic properties of nanoparticles are very different from those of bulk materials.
- Nanosize increases the surface area of the material; nanoparticles are more reactive than bigger particles of the same material, their melting point reduces, conductivity of metals changes from conductor to semiconductors and even insulators, tensile strength increases, non-magnetic substances such as gold exhibit magnetism at the nano level and even the color of nanosize is different from that of material at the bulk level.
- Nanomaterials can be prepared in two ways
 - By dividing bulky materials into nanosize particles (top-down approach).
 - By assembling small particles to form nano-sized particles (bottom-up approach).
- Self-assembly is the basic principle underlying the bottom-up approach where small particles aggregate on their own without the aid of any external force to form ordered patterns.
- The driving force behind self-assembly are van der Waals forces, electrostatic forces, hydrophobic interactions, π - π interactions, hydrogen bonds, metal-ligand bonds, etc.
- Molecules assemble to form molecular self-assembly whose properties are different from the individual molecules.
- Material self-assembly is made of individual blocks of nanoparticles.
- Self-assembled mono layers (SAM) are formed by the adsorption of active surfactants on a solid surface.
- Mesoscale self-assembly (MESA) varies from 10 nm to 10 mm (1 cm). The additional forces participating in MESA are capillary, electrostatic, magnetic, optical, gravitational, etc.
- MESA can be prepared by
 - Capillary interactions
 - Spontaneous folding
 - Hierarchical self-assembly
 - Templated self-assembly
 - Changing solvent polarity
 - Dynamic self-assembly.

- Nanomaterials can be prepared by
 - Mechanical grinding
 - ◊ Wet chemical synthesis (sol–gel process)
 - ◊ Gas phase synthesis (chemical vapor deposition).
 - Chemical vapor deposition is achieved in a number of ways
 - ◊ Furnace heating
 - ◊ Flame-assisted ultrasonic spray pyrolysis
 - ◊ Gas condensation processing (GCP)
 - ◊ Chemical vapor condensation (CVC)
 - ◊ Sputtered plasma processing
 - ◊ Microwave plasma processing.
- Important nanomaterials are carbon nanotubes (bucky tubes), nanocrystals, nanowires of carbon, quantum dots and nanocones.
- Nanomaterials find extensive application in the field of medicine (both diagnosis and treatment and as drug carriers), as catalysts, for control of environmental pollution, in electronics, in mechanics to improve the strength of materials, in cosmetics, in surface science, as lubricants, etc.

Review Questions

1. Define nanochemistry. Explain with the help of suitable examples how the properties of nanomaterials differ from those of the same materials in bulk size.
2. What do you understand by the term ‘self-assembly’? Explain the fundamental principles of self-assembly.
3. What are molecular self-assembly and material self-assembly? Explain.
4. What do you understand by mesoscale self-assembly (MESA)? Write down the different methods used to construct MESA and also compare MESA with molecular self-assembly.
5. What are nanomaterials? Write down the various methods used for the preparation of nanomaterials.
6. Explain the following
 - (i) Carbon nanotubes
 - (ii) Nanocrystals
 - (iii) Nanowires
 - (iv) Nanocones
 - (v) Haecalites

7. Write the various applications of nanomaterials in the following fields
 - (i) Medicine
 - (ii) Catalysis
 - (iii) Environment technology
 - (iv) Electronics
 - (v) Mechanics and
 - (vi) Other miscellaneous uses.

Multiple Choice Questions

1. Nanoscience deals with materials whose size ranges from
 - (a) 1–10 nm
 - (b) 10–100 nm
 - (c) 100–1000 nm
 - (d) >1000 nm
2. Nanomaterials differ from bulk materials in their
 - (a) Electrical properties
 - (b) Magnetic properties
 - (c) Optical properties
 - (d) All the above
3. Bulk gold is a conductor and is non-magnetic but at nanosize it becomes
 - (a) Insulator and non-magnetic
 - (b) Conductor and magnetic
 - (c) Semiconductor and magnetic
 - (d) Semiconductor and non-magnetic
4. Molecular self-assembly does not involve which of the following forces
 - (a) van der Waals forces
 - (b) π – π interactions
 - (c) Hydrogen bonds
 - (d) Capillary forces
5. The size of mesoscale self-assembly (MESA) varies from
 - (a) 10–10 mm (1cm)
 - (b) 1–10 nm
 - (c) 10–50 nm
 - (d) 50–100 nm
6. Which is not an example of the bottom-up approach for the synthesis of nanomaterials
 - (a) Chemical vapor condensation
 - (b) Mechanical grinding
 - (c) Microwave plasma processing
 - (d) Chemical vapor deposition
7. Carbon nanotubes are considered as
 - (a) 0D structure
 - (b) 1D structures
 - (c) 2D structures
 - (d) 3D structures

8. The symmetry and helicity of CNT about the tube axis affect their
 - (a) Electronic properties
 - (b) Mechanical properties
 - (c) Both electronic and mechanical properties
 - (d) Neither electronic nor mechanical properties
9. Which of the following is not a one-dimensional nanomaterial
 - (a) Carbon nanotubes
 - (b) Nanowires
 - (c) Nanocones
 - (d) Langmuir–Blodgett (LB) film
10. A layered structure of pentagons, hexagons and heptagons that can be rolled like CNTs is
 - (a) Haeckalites
 - (b) Nanowires
 - (c) Graphene
 - (d) Dendrimers
11. Nanomaterials are used in medicine as
 - (a) Drug carriers
 - (b) For diagnosis
 - (c) For treatment
 - (d) All of the above
12. Nanoparticles are used
 - (a) To improve performance of tyres
 - (b) For lubrication
 - (c) In data storage devices such as computer hard discs
 - (d) All the above

Solutions

- | | | | | | | | |
|-------|--------|--------|--------|-------|-------|-------|-------|
| 1 (b) | 2 (d) | 3 (c) | 4 (d) | 5 (a) | 6 (b) | 7 (b) | 8 (a) |
| 9 (c) | 10 (a) | 11 (d) | 12 (d) | | | | |

CHEMICAL ASPECTS OF BIOTECHNOLOGY

24.1 Introduction

Biotechnology is technology based on biology in which cells of living organisms like bacteria, viruses, fungi, yeast, plants and animals are used to modify various processes and produce useful products. The UN Convention on Biological Diversity, Part 2, defines biotechnology as ‘any technological application that uses biological systems, living organisms or derivatives thereof to make or modify products or processes for specific use’. The word ‘biotechnology’ owes its origin to two Greek words *bios* meaning ‘pertaining to life’ and *technikos* meaning ‘involving human knowledge and skills’.

The science of biotechnology is not new although its systematic study and scientific applications started only a few decades ago. There are evidences in history to prove that biotechnology was used even thousands of years ago in ancient times to produce foods like bread by adding yeast, for the preparation of beverages like beer and wine by the fermentation of various grains and fruit juices, to convert milk into curd, cheese and yogurt, in the field of medicine, in *ayurveda*, for strengthening the immune system, selective breeding to improve the quality of crops and livestock by mating organisms of desired characteristics to produce offsprings with specific features.

The modern aspect of biotechnology includes genetic engineering where genes are modified to develop special traits within individuals, to make them disease resistant, increase productivity, produce high yielding variety of crops, develop food products, fruits and vegetables that are more nutritious, disease-resistant and taste better than the conventional food items. Other tools of modern biotechnology are tissue culture and molecular breeding which help to improve the quality and productivity of plants and animals, increase their commercial value and make them more useful for man and society.

24.2 Applications of Biotechnology

Biotechnology is an applied science with multiple applications in various fields like agriculture, medicines, textiles, paper and pulp, mining and metal refining, waste management, energy sector, food processing, livestock management in marine and aquatic life, forestry, industrial sector, etc.

The main applications of biotechnology are discussed here.

(i) **Biotechnology in agriculture** The application of biotechnology to agriculture is called *green biotechnology*. The use of biotechnological tools can increase the production of crops, develop high yielding and more nutritious crops, improve their resistance to diseases and adverse conditions like drought, develop insect protected biotech crops and thereby reduce the use of chemical pesticides and fertilisers. All this can be achieved by the use of genetic engineering. The crops can be modified genetically to produce special traits which normally do not exist in them. Harmful genes can be isolated and special genes can be introduced in the plant. Genetic modification has led to the production of crops which have the following advantages.

- They ripen easily on the plant itself.
- Fruits and vegetables have a better shelf life.
- The crops have an improved nutritional profile. For example, the nutritional status of tomato has been improved by introducing nutrients such as vitamin C, vitamin E or beta carotene in it.
- ‘Golden rice’ with an increased content of iron and vitamin A has been designed. It was developed to fight the problem of malnutrition in underdeveloped countries. Brazil nuts, *Berthalletia excelsa* contains sulphur-rich protein. This protein contains two nutritionally important sulphur containing aminoacids – methionine and cysteine. Although soyabeans and other legumes have high protein content, they are deficient in this sulphur-rich protein. Hence, the sulphur-rich protein gene has been transferred to soyabeans to improve their nutritional value.
- Genetic modification has produced crops which require less pesticides and fertilisers, are more disease resistant and require less water so that they can combat conditions of drought. For example, *glyphosate* is a powerful, effective and environmentally safe herbicide, but it kills both weeds and crops indiscriminately. Therefore, biotechnologists isolated a glyphosate resistant gene from the bacterium *Salmonella typhimurium* and successfully transferred it into cotton, soyabeans, tobacco and tomatoes so that these crops become resistant to glyphosate.
- Biotechnological processes help to reduce toxins in plants like cyanide in cassava.
- Genetic modifications can help in developing plants which have higher contents of oil, starch, gum and resin as required.
- A bacterium *Bacillus thuringiensis* (in short Bt) produces proteins called cry proteins which is toxic to larvae of various insects like tobacco budworm, beetles, mosquitoes. The genes of this protein have been isolated from this bacterium and introduced in various plants like cotton, tomato, rice, soyabean to create Bt cotton, Bt tomato, Bt rice, Bt soyabean, etc. The protein makes the plant pest resistant. It exists in inactive protoxin form in the plant and when ingested by the animal gets activated and kills it.

(ii) **Biotechnology in medicine** Biotechnology applied to medical processes is termed as *red biotechnology*. The application of biotechnology in medicine helps in the diagnosis, prevention and cure of various diseases. A biotechnological tool helps to decipher the genetic sequence of individuals and diagnose their vulnerability to various hereditary diseases. The study of

genes and chromosomes helps in the timely detection of various inherited disorders and the likelihood of their expression in an individual.

Gene therapy, that is, altering DNA within the cells is one of the most promising areas of biotechnology that has been used to prevent the occurrence of and cure serious ailments like cystic fibrosis, AIDS and cancer.

Microorganisms have been used for therapeutic purposes also. Various antibiotics (Greek, *anti* meaning against and *bios* meaning life), antiviral drugs, antifungal drugs, antibacterial drugs have been developed with the help of microorganisms. In these drugs, chemical substances excreted by microorganisms inhibit the growth and development of microbes. Pneumonia caused by *Streptococcus pneumonia* can be treated by penicillin; leprosy by *Leptrae bacilli* is treated by dapsone and rifampicin. Vaccines have been developed for diseases like smallpox; various viral infections can be prevented by the use of vaccines. The vaccines commonly used for human beings are those for rubeola (also known as measles), rubella, poliomyelitis and influenza. Immunisation with a virus vaccine stimulates the body's immune mechanism to produce a protein – called an antibody – that will protect against infection by the immunising virus. The virus is altered before they are used for immunisation so that they cannot themselves produce disease. Antifungal drugs like fluconazole or clotrimazole and antiprotozoal drugs are also developed from microorganisms. These drugs disrupt the chemical structure of the cell membrane in fungi and protozoa, thereby preventing the absorption of vital nutrients and allowing toxins into the fungal cell.

Similarly, the use of biotechnology has helped to produce insulin by inserting the DNA sequence of human insulin into the plasmids of a harmless strain of *Escherichia coli*. This has enabled the production of insulin at a low cost. Earlier, it was extracted from the pancreas of animals like cattle and pigs.

DNA fingerprinting helps in establishing parenthood in children. Samples of DNA from hair, skin and body fluids are very useful in various criminal investigations also.

- (iii) **Biotechnology in animal husbandry** From the very ancient times, people have improved animal productivity and breeding by selecting the best animals. The use of biotechnology tools and study of reproductive biology and genetic basis of traits have given new tools to researchers to accomplish their objectives. Artificial insemination has revolutionised animal breeding; biotechnology has been applied to animal husbandry by developing vaccines to prevent them from diseases. Embryo transfer from livestock has changed the nature of cattle breeding; several calves can be produced from one embryo by cloning. Research has helped in the production of animal growth hormones to increase their growth rate and productivity. For example, bovine growth hormone (BGH), a naturally occurring hormone increases milk production in cows, porcine growth hormone (PGH) stimulates the growth rate in pigs and increases the ratio of muscle to fat. Growth hormones offer great benefits for a variety of meat animals like poultry and fish.

Another important aspect of biotechnology in animal agriculture is in the diagnosis, prevention and control of animal diseases. Every year, thousands of poultry animals die due to various bacterial and viral infections. Preventive vaccines have been developed and administered to animals to protect them against virus that cause diseases like fowl plaque, influenza, vesicular stomatitis, foot and mouth disease and rabies.

Biotechnology can also be applied to marine and aquatic life – *blue biotechnology*. Aquatic organisms are a good source of protein rich food. Transfer of growth genes into fish is being viewed as a major means to increase the available protein. Genetic engineering can be applied to improve the production of fish, their quality, survival and growth rate, disease resistance and meat quality. This advancement is termed as *blue revolution*.

- (iv) **Biotechnology in environment** Environmental pollution is a global problem which results in the decline of the environmental quality. Biotechnology has played a vital role in curbing the menace of pollution and promoting sustainable growth.

This has happened in two ways. Firstly, biotech crops and genetically engineered plants require less fertilisers and pesticides. This decreases the concentration of fertilisers and pesticides in the land, soil and water bodies and also reduces the pesticide residues in food products. Increased productivity of biotech crops lessens the encroachment of land for agriculture. Secondly, microorganisms feed on various organic, inorganic and toxic substances present in nature and convert them into harmless end products. They can thus be used to clean the environment. Bioremediation, an application of environmental biotechnology, is widely being used for environmental protection. The microorganisms listed in Table 24.1 help in cleaning the environment.

Table 24.1 Role of microorganisms in controlling pollution

Microorganisms/Enzymes	Function
Hypomicrobium	Grown in the presence of ethanol; it reduces nitrates in waste water
Oxido-reductase enzyme in the presence of electric current	Reduce nitrates in waste water
Immobilised cells of <i>Nitrosomonas europaea</i>	Oxidise ammonia to NO_2 and NO_3
Immobilised α -amylase enzyme	Used to clarify colloidal starch, clay suspensions from paper mill industry and also to treat waste water from wheat starch industry
Fungus <i>Aureobasidium pullulans</i> or <i>Pseudomonas</i> spp.	These when adsorbed on fibrous asbestos or anthracite coal help to remove phenols from waste water of hospitals and laboratories
Microbes like <i>Bacillus</i> , <i>Vorticella</i>	Break down organic matter to carbon dioxide and water in an activated sludge digester or trickling filter
Microbes from the intestinal tract and other anaerobic bacteria	Digest sludge in septic tanks
Different strains of <i>Pseudomonas</i>	They consume hydrocarbons and help in cleaning water contaminated with oil
<i>Zoogloea ramigera</i>	It removes copper from factory waste and also has the potential to remove toxic wastes including uranium
Bacterium like <i>Alcaligenes eutrophus</i>	Help to degrade plastic
Fungi like <i>Penicillium</i> and <i>Aspergillus</i>	Remove carbon monoxide from air by converting it into CO_2

(v) Biotechnology in energy

Conventional fuels like coal, petrol, diesel and kerosene are fossil fuels which are limited in nature. These energy resources are dwindling fast. Bioenergy can play an important and vital role in solving the energy crisis of the world. Biomass and residues from plant and crop material like paddy straws, rice husk, bagasse, corn cobs, animal droppings, cow dung and animal dung, forest based residues like bark, saw dust, wood shavings can be converted into energy by processes like incineration, pyrolysis, anaerobic digestion, gasification, etc.

Beside this, there are some plant species that yield a mixture of hydrocarbons. They are termed as the petroplants or petroleum plants. *Jatropha curcas* is the most common example of petroplant used to derive biodiesel. Similarly, in Italy, vegetable gasoline is obtained from *Euphorbia*. The latex of *Aak* (*Calotropis procera*) contains hydrocarbons in which the C and H ratio is similar to crude oil, fuel oil and gasoline. This plant can be used as a substitute of petroleum. Some algae produce hydrocarbon and methane that can be used as biofuels. *Spirulina*, a cyanobacterium, is also a good source of methane. It can be used for methane production by anaerobic digestion. These biofuels are a cheap and clean source of energy and do not cause pollution.

(vi) Biotechnology for biofertiliser production

Biofertilisers contain microorganisms which utilise biological processes to mobilise the conversion of elements from non-usable form to usable form. Bacteria like *Rhizobium* present in the root nodules of leguminous plants convert atmospheric nitrogen directly into nitrates. These symbiotic bacteria can be cultured on manitol agar and can be used as biofertilisers or microbial inoculants. Similarly, *Azotobacter* inoculant or biofertiliser fixes nitrogen and is capable of producing antibacterial and antifungal compounds and hormones. *Blue green algae* or *cyanobacteria* is a photosynthetic nitrogen fixer and its use as a biofertiliser in rice gives promising results. A large number of biofertilisers have been prepared which mobilise the absorption of various nutrients and improve the growth and productivity of plants.

(vii) Biotechnology in industries

It is also known as *white biotechnology* and deals with the application of the principles of biotechnology in industrial processes to:

- Reduce the adverse environmental impacts of various manufacturing processes.
- Devise more efficient manufacturing processes such as cleaning, bleaching paper and pulp; recovery of minerals from effluents; waste water treatment.
- Devise more energy efficient processes by the use of microorganisms.
- Produce more useful and eco-friendly products like detergents, biodegradable plastics, food articles, chemicals and textiles.
- Use biocatalysts or enzymes to enable reactions to occur under mild conditions or in ambient conditions.

Bio-based industrial processes are environment friendly and cost effective although broader and widespread commercial application of biotechnology to industrial processes is still in the infant stage. Various important industrial applications of biotechnology are explained here.

(a) Mining and metal refining

- Copper can be liberated from sulphide ore by bioleaching in which the sulphur and iron present in the ore are oxidised by naturally occurring bacteria at ambient temperature. The process is carried out at mine sites, whereas conventionally, the ore has to be transported to the smelter where the impurities are removed at high temperature. Bioleaching process is cheaper, environment friendly and presently accounts for 20%–25% of the world copper production.
- A bioprocess has been developed to recover zinc and other metals like tin, copper, nickel, manganese, etc. The metal is treated with lime or limestone which produces gypsum contaminated with heavy metals. In the bioprocess, sulphate reducing bacteria trap zinc and other metals from waste water and precipitate them as metal sulphides which are then recycled back into the refinery feedstock.

(b) Green plastics

- Renewable agricultural feedstock ‘corn’ has been used to produce a biopolymer, polylactic acid (PLA), using bioprocess. This polymer can be used as a substitute for plastics like nylon, PET, polyester and polystyrene. It is biodegradable and can also be composted.
- Similarly, genetically modified cotton containing a bacterial gene produces a polyester like substance having the texture of cotton but which is warmer and biodegradable. Genetically modified plants and microbes produce polyhydroxybutyrate, a feedstock for producing biodegradable plastics. Through microbial fermentation, genetic engineering has also led to the production of natural protein polymers such as spider silk and adhesives from barnacles.

24.3 Biocatalysts or Enzymes

Biocatalysts are catalysts derived from living organisms.

Characteristics of enzymes

1. They acts as catalysts and alter the rate of a reaction without themselves participating in the reaction.
2. Like inorganic catalysts, they do not disturb the final equilibrium of the process. They only help to achieve the equilibrium faster.
3. If the concentration of a reactant is small, then the rate of reaction is proportional to the concentration of the enzyme. At a high reactant concentration, the rate of reaction is independent of the enzyme concentration.
4. Enzymes are highly specific in nature. A particular enzyme acts on a specific substrate, like zymase converts cane sugar or beat sugar to alcohol; it cannot ferment malt sugar or maltose.

5. Enzymes are very sensitive to pH and temperature. They exhibit maximum reactivity in the temperature range 25–30 °C. They are destroyed by ultraviolet light and heat. They become inactive at low temperatures.
6. The activity of enzymes can be increased by adding other substances called coenzymes which act as promoters. On the other hand, enzyme activity may be destroyed by inhibitors like boric acid, mercuric salts, ammonium molybdate, etc.
7. A very small quantity of enzyme can bring about the decomposition of a large quantity of the substrate. For example, a part of urease extracted from soyabean catalyses the hydrolysis of 10 million parts of urea.

Industrial biotechnology uses biocatalysts in the food industry, dairy industry, paper and pulp industry for bioleaching, more efficient recovery of oil and gas and in chemical synthesis. A few of these industrial applications are discussed below.

- (a) *Food industry*: Enzymes have widespread applications in the food industry. *Amylase* is used to produce sugar from starch. *Proteases* help in lowering the protein level of flour during the manufacture of biscuits and for softening meat. *Trypsin* is used to prepare predigested baby food. *Amylases*, *amylglucosidases* and *glucoamylases* convert starch into glucose and various syrups; *yeast* fermentation raises dough.
- (b) *Beverage industry*: *Carbohydrases* and *zymase* are used for the preparation of alcohol by fermentation, *proteases* remove cloudiness from alcohol; *cellulases* and *pectinases* are used for fruit juice processing, *amylases*, *glucanases* and *proteases* break the polysaccharides and proteins in malt.
- (c) *Dairy industry*: *Rennin* and *pepsin* derived from stomach of calves and lambs are used to manufacture cheese; *lactases* break lactose to glucose and galactose.
- (d) *Paper industry*: *Ligninases* remove lignin to soften paper; *xylanases* reduce the amount of bleach required for decolourising paper (process called biobleaching); *cellulases* make the fibres smooth and help in the removal of ink.
- (e) *Miscellaneous uses*: *Proteases* are used for contact lens cleaning; they dissolve gelatin from scrap film and allow the recovery of silver content; *amylases* and *proteases* are used in detergent to remove starch and protein residues; *lipases* used in detergents help in the removal of fatty and oily stains, *cellulases* act as fabric conditioners; *peroxidases* are used in laundries for biobleaching.

24.4 Fermentation

The term ‘fermentation’ (Latin *fervere* meaning ‘to boil’) was initially associated with the decomposition and rotting of food stuffs. It is now considered to be a physiological process in which microorganisms like bacteria and fungi metabolise the substrate with the help of enzymes to produce sugars, acids, alcohols and gases. Souring of milk and kneaded flour, curdling of curds, fermentation of batter for the preparation of *idli* and *dosa*, conversion of fruit juices and sugars into wine, rotting of fruits and vegetables, putrefaction of meat are common examples of fermentation in day-to-day life. Fermentation also occurs in the stomach of animals, during respiration and in mammalian muscles.

Although the fermentation of fruits and grains to make alcohol and beverages has been established for centuries, the wider and industrial applications of the phenomenon are being recognised now. The life processes of microorganisms like bacteria, yeast and moulds is being utilised to manufacture large number of chemicals like alcohol, acetone, acetic acid, lactic acid, citric acid, antibiotics and vitamins which are of great synthetic and industrial significance. Fermentation is also used to cure tea leaves, tobacco; produce indigo dye, coffee; prepare benzaldehyde or oil of bitter almonds from amygdalin contained in the almond seed, preserve sour food like pickled cucumbers. The scientific nature of the process was established in 1822 by Louis Pasteur, who considered it a type of physiological oxidation carried out by living organisms in the absence of air. Later in 1860, he demonstrated that bacteria were responsible for the souring of milk. He studied the role of microorganisms in the spoilage of food and this led to the discovery of the process of pasteurisation.

Conditions favourable for fermentation

Fermentation is an enzymatic process influenced by various factors. The factors include the following.

- (i) *Temperature* The optimum temperature for fermentation is 25–35 °C. At high temperature, the enzymes are destroyed and at low temperature, generally below 20 °C, they become inactive and the process becomes very slow.
- (ii) *Concentration* High concentration of the solution renders the enzyme inactive. The process proceeds at an optimal rate only in sufficiently dilute solutions.
- (iii) *Presence of other substances* Since the process is carried by microorganisms, any substance which provides nourishment to the microorganism speeds up the process. Inorganic salt solutions act as food for them and assist the process. However, if the other substance destroys the ferment (microorganisms) or reduces its biological activity, then the process of fermentation is retarded. Substances like boric acid, ammonium molybdate reduce or even stop fermentation and are used as preservatives.
- (iv) *Aeration* Although fermentation occurs under anaerobic conditions, the process occurs fast under well-aerated conditions.

24.5 General Outline of the Fermentation Process

Fermentation can be carried out both under aerobic as well as anaerobic conditions. Both types of processes require suitable raw material and microorganisms. The raw material can be fruits like grapes, apples; grains like wheat, barley, rice; industrial byproducts like molasses, etc. The microorganisms used for fermentation depends on the raw material to be fermented. They can be bacteria, yeast or moulds which are cultured and maintained. After the selection of the microorganisms and the raw material, the medium is prepared.

Preparation of the medium: Before subjecting the raw material to microbial action, it is treated physically and chemically. Fruits are sliced, crushed and pressed to extract their juices; sugars and molasses are dissolved in hot water. They are then clarified by filtration and centrifugation. The

medium is sterilised at a temperature of 120–130 °C for about 15 minutes. Then the microorganisms called inoculums are added.

Fermentation process: It is carried out in a vessel called the fermenter or the bioreactor. The fermenter is designed to maintain both aerobic and anaerobic conditions, desired temperature, pH, culture in pure state throughout the process to support the growth of microorganisms for optimum formation of products. It should be equipped with proper agitation and aeration facility, evaporation should be less, the inner surface should be smooth and the vessel must operate with minimal use of labour.

Both batch and continuous process is employed, although the batch process is widely used. In the batch process, the microorganism is 'seeded' into the culture medium. The inoculums which are normally not more than 5%–10% of the total culture volume is aseptically transferred to the fermenter with the help of a sterile, disposable syringe. The optimum conditions are maintained, fermentation proceeds and the product is then harvested. The fermentation time depends upon the nature of the culture medium and may vary from a few days to several months.

The pH and temperature are maintained by automatic controlling devices. In aerobic fermentation, the presence of oxygen is necessary and a proper supply of air is to be maintained. After the completion of the process, the product is harvested and a fresh batch of culture medium and inoculums is introduced into the fermenter.

In the continuous fermentation process, the sterile medium is continuously fed at one end of the fermenter and the fermented product is continuously withdrawn from the other end, maintaining a constant fermentation volume throughout the process.

Batch process is generally preferred over continuous process for industrial fermentations.

24.5.1 Manufacture of ethyl alcohol by fermentation

The important raw materials for the manufacture of ethyl alcohol are saccharine materials like molasses, sugar beets, sugarcane, starchy materials like starch, potatoes, maize, barley, rice and cellulosic materials like sulphite liquor from paper mills.

Ethyl alcohol from molasses

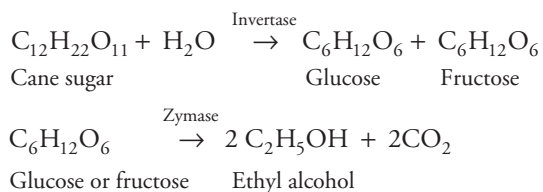
Molasses is the dark coloured viscous liquid left after the crystallisation of cane sugar or beet sugar. It contains about 55% sugar (cane sugar, glucose and fructose) out of which about 35%–40% is cane sugar or sucrose. The various steps involved in the process are given below.

Preparation of wash

Molasses cannot be fermented as such because the concentration of sugar is very high. Therefore, it is diluted to obtain a solution with 8%–10% sugar concentration. A small amount of dilute sulphuric acid is added to check the growth of undesirable bacteria (which would otherwise form lactic acid and acetic acid) and to adjust the pH to 4.5–5.0. A small amount of ammonium phosphate or ammonium sulphate is added to act as food for the yeast cells. The resulting solution is called a mash.

Fermentation Mash is then pumped into a large steel fermenter. Yeast (about 5% of the total volume) is added to the fermenter and the temperature is maintained at 30 °C. The mixture is

allowed to stand for a few days. The reaction is exothermic and cooling coils are employed to maintain the required temperature. The enzymes present in the yeast convert sucrose and other sugars to ethyl alcohol. The reaction occurs as follows.



The fermentation time varies from 36–50 hours and the carbon dioxide liberated in the process is scrubbed with water and either disposed off or sold as dry ice. Air is passed to arrest the process of fermentation. The yeast is filtered off and the filtrate thus obtained is called wash or wort and contains 6%–10% alcohol.

Fractional distillation:

The wash or wort contains about 6–10% ethyl alcohol, 3–5% glycerol, higher alcohols, acetaldehyde, etc. It is subjected to fractional distillation in a specially designed continuous still called the *Coffey still* which consists of two tall fractionating columns called the *analyser* and the *rectifier* (Fig. 24.1).

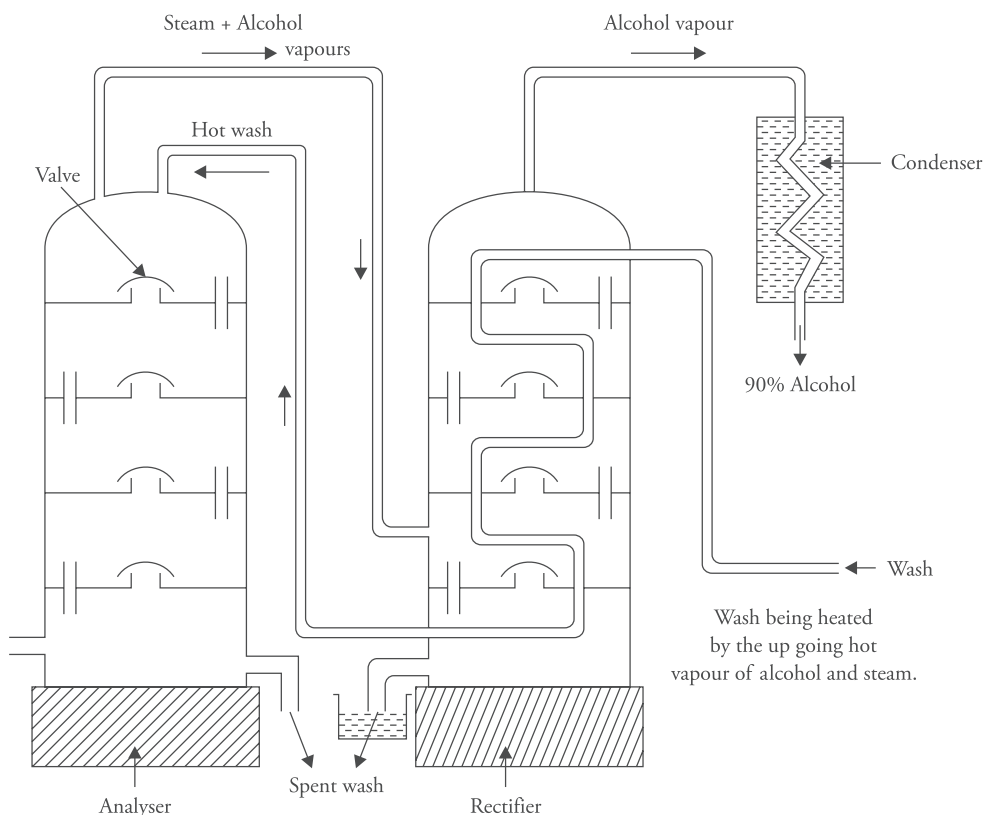
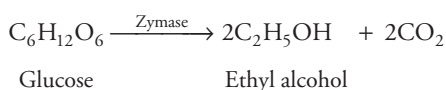
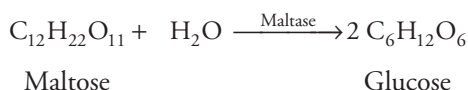
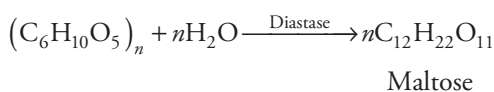


Figure 24.1 Fractional distillation of wash in a Coffey still

The columns are provided with perforated horizontal plates having valves opening upwards. The Coffey still works on the counter-current principle in which steam and alcohol travel in opposite directions. Wash containing 6%–10% alcohol is pumped through the upper section of the still after passing through several heat exchangers. Steam is introduced from the bottom of the analyser. The steam rises up and carries with it the vapours of alcohol from the descending wash. A mixture of alcohol and steam vapours leaves the analyser at the top and enters the rectifier at the bottom. In the rectifier, the steam condenses and the vapours of alcohol escape from the top. They are then condensed with the help of a condenser. This alcohol is 90% pure. The liquid collected at the bottom is spent wash. The pure (90%) alcohol is then subjected to fractional distillation. Low boiling liquids like acetaldehyde are obtained in the first fraction, the second fraction contains 95% alcohol and is called rectified spirit or industrial alcohol and the last fraction contains fusel oil (a mixture of n-propyl, n-butyl, n-amyl, isoamyl and optically active amylalcohols).

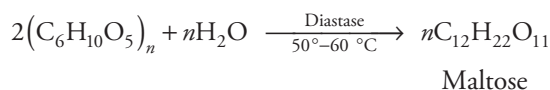
Alcohol from starch

In this method, a starchy mash is prepared which is then mixed with malt and yeast. This produces enzymes for fermentation.

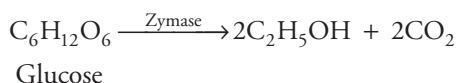
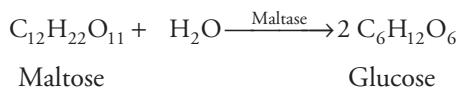


The process is illustrated here with potato as the starting material:

- (i) *Preparation of mash* The potatoes are cut into thin slices and cooked in high pressure steam to form a gelatinised starchy mash.
- (ii) *Saccharification of mash* Saccharification is the process of converting starch into maltose. It is completed in two steps.
 - (a) *Preparation of malt* The barley grains are cleaned and soaked in water for 3–4 days. Water is then drained off and the moist grains are allowed to germinate in the dark for 10–13 days. The germinated barley seeds (called malt) are dried at 30–35 °C for 48 hours and then heated in a kiln at 70–95 °C to stop germination without destroying the enzymes. The seeds are then crushed, extracted with water and filtered. The filtrate contains the enzyme diastase and is called the malt extract.
 - (b) *Preparation of wort from mash by the action of malt* Malt extract is added to mash at 50–60 °C. The mixture is kept for half an hour wherein the hydrolysis of starch to maltose takes place.



Fermentation of sterilized wort Yeast is added to the wort containing 40% starch, 30% barley malt and 30% long fibre malt sprouts. The pH is maintained at about 4.5–5.0, the temperature at 25–30 °C and the mixture is kept for 2–4 days. Fermentation proceeds and the reaction being exothermic the temperature rises but is maintained at 30 °C by the use of cooling coils. The enzyme maltase, present in yeast, hydrolyses maltose into glucose while zymase, also present in yeast, converts glucose to ethyl alcohol.

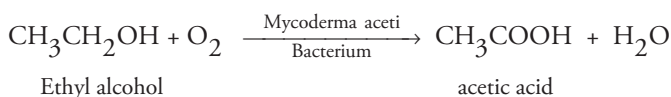


- (iii) **Distillation and rectification of fermented liquor** After this, the ethyl alcohol is distilled and rectified as described earlier.

24.5.2 Manufacture of acetic acid by fermentation

It is observed that sometimes alcoholic beverages like wines become sour when exposed to air for some time. This is due to the oxidation of alcohol to acetic acid in the presence of certain fungi and bacteria, like, *Mycoderma aceti* and *Bacterium aceti*. The process is utilized to prepare vinegar which is a dilute solution of acetic acid containing 5.5%–10% acetic acid. Vinegar stronger than 14% cannot be prepared as the bacteria causing fermentation are killed in concentrated solutions.

Fermentation is done by the bacterium *Mycoderma aceti* in the presence of air at 30–35 °C



The process is carried out in large wooden vats having perforated covers at the top and bottom for the passage of air (Fig. 24.2). The vat is filled with wooden shavings soaked in old vinegar which contains the bacterium *Mycoderma aceti*. Dilute alcoholic solution containing growth nutrients like phosphates and inorganic salts gradually trickles down on the shavings and air enters from the bottom. The alcohol is fermented in the presence of the bacterium. Fermentation is an exothermic process, hence it is important to maintain the temperature at 30–35 °C. The dilute acetic acid from the first vat is made to trickle down. Many such vats are kept in series till the desired concentration is obtained.

Freshly prepared vinegar lacks the usual flavour of vinegar; hence it is stored for nearly 6–12 months. After proper aging, vinegar is clarified, filtered, pasteurised and finally packed.

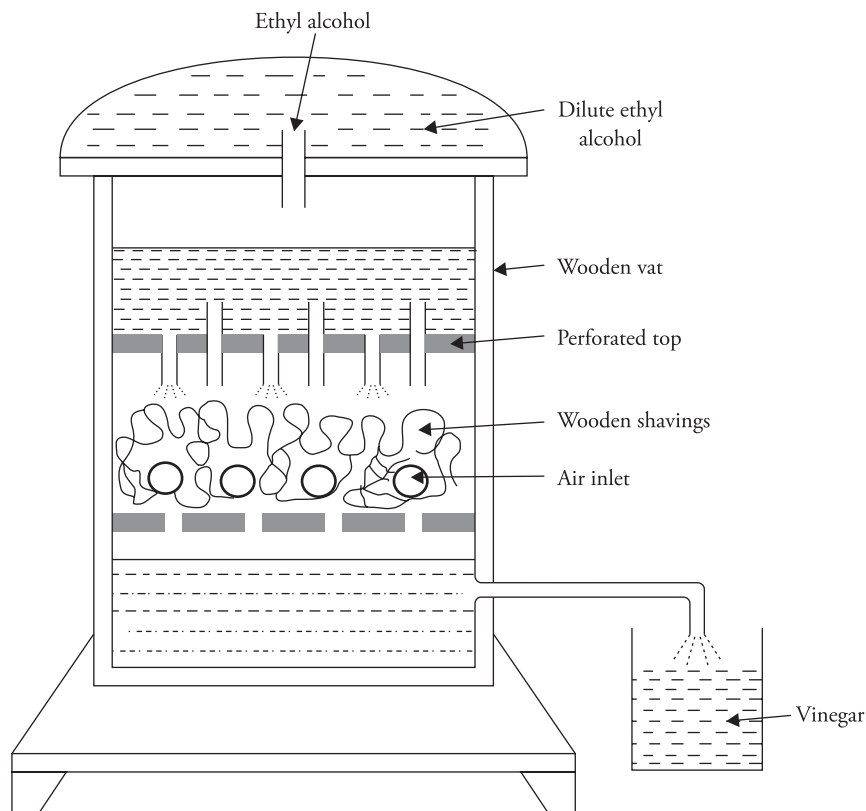


Figure 24.2 Preparation of acetic acid by quick vinegar process

24.5.3 Manufacture of some other products by fermentation

1. **Citric acid** It is prepared by the fermentation of beet molasses using the fungus *Aspergillus niger*. Pure sucrose and highly refined syrups can also be used as the fermentation medium. Highly aerobic conditions are maintained. The cultures are aerated with sterile air and agitated at a temperature of 25 to 30 °C for 7 to 10 days. The pH is kept below 3.5 and nitrogen is provided by adding ammonium salts. Copper and organic ions are added to control mycelial growth and increase citric acid production. Lime is added to the culture medium to precipitate any oxalic acid formed, and mycelium and calcium oxalate are filtered off. The citric acid thus formed is precipitated and purified by re-crystallisation from water.
2. **Lactic acid** It is prepared by the fermentation of sugars with *Lactic bacilli* present in sour milk or decaying cheese. Powdered chalk is added to neutralise the acidity and keep it below 1% as high acidity deactivates the fungi. The temperature is maintained at 37–42 °C. The calcium lactate crystals formed are separated and removed. Free acid is obtained from calcium lactate crystals by treating it with dilute sulphuric acid, where calcium sulphate precipitates out and is filtered off. The free lactic acid is obtained from the filtrate by distillation under reduced pressure.

3. **Acetone** It can be prepared by the fermentation of starch or molasses with the microorganism *Clostridium acetobutylicum*. The products of the fermentation reaction are butanol, acetone and ethanol in the ratio 6:3:1 which are separated and purified by fractional distillation. Carbon dioxide and hydrogen are also evolved in the process.
4. **Vitamins** Vitamins are organic substances essential in small amount for the health, growth and maintenance of the body.

Vitamin B₁₂ (cyanocobalamin) Various microorganisms like *Pseudomonas* (*P. denitrificans*) and *Propionibacterium* (*P. Shermanii* and *P. freudenreichii*) are used for the commercial production of vitamin B₁₂. The culture media consists of sugar beet molasses containing 5%–10% betaine (trimethyl glycine), which stimulates the production of vitamin B₁₂, yeast, ammonium phosphate and other inorganic salts. The pH is maintained at 7.4 and the temperature is about 29 °C. The inoculum is well aerated in a bioreactor and the culture is incubated for about 90 hours resulting in the production of vitamin B₁₂.

Vitamin B₂ (riboflavin) It is produced from the bacteria *Clostridium acetobutylicum* and *Candida flaveri*. The bacterium *Ashbya gossypii* can also accumulate large amounts of riboflavin. For the production of the vitamin, a suitable carbohydrate containing mash is prepared, sterilised and inoculated with the suitable bacterium at 37–40 °C for 2–3 days. The pH is adjusted to 6–7 and the mass is buffered with calcium carbonate.

Vitamin C (ascorbic acid) Commercially, vitamin C is obtained by semi-synthesis from D-glucose. It occurs in two steps. The first step involves the fermentation of D-glucose to 2-keto-L-gluconic acid using *Bacillus thurigiensis*. The other strains of bacterium used for fermentation are *Corynebacterium sp* and *Erwinia sp*. The 2-keto -L-gluconic acid produced in the first stage is further processed chemically by lactonisation and isomerisation to yield L-ascorbic acid.

Production of Antibiotics

Penicillin: It was originally isolated from *P. notation* which gave low yields of penicillin. *P. chrysogenum* is used these days as it gives superior yields of penicillin. Spores of *P. chrysogenum* are developed from the vegetative mycelium and added to flasks containing wheat bran and nutrient solutions. The pH is maintained between 6.8 and 7.4 while the temperature is maintained between 23 °C and 25 °C. It is incubated for 5 to 6 days and after incubation, the mycelium is filtered from the liquid medium. It contains penicillin and is mixed with suitable solvent, centrifuged and crystallised.

Other antibiotics: Streptomycin, tetracyclines, chloramphenicol and various other important antibiotics can be prepared by the fermentation process.

Summary

- Biotechnology is the science that uses living organisms to modify various processes to produce more useful products.
- Biotechnology applied in different fields is known as
 Green Biotechnology → Agriculture
 Red Biotechnology → Medicine
 Blue Biotechnology → Aquatic and marine life
 White Biotechnology → Industries
- Biotechnology uses various tools like genetic engineering, tissue culture and microbiology to produce high yielding, more nutritious, disease resistant variety of crops; in medicine, it helps in the timely detection and cure of diseases, development of antibiotics, protection against viral diseases, in animal husbandry, it has helped to produce high milk and meat producing animals.
- Biotechnology has helped in the sustainable development of environment by reducing the use of fertilisers, pesticides, microbial treatment of waste products. It has assisted the energy sector by the production of biofuels.
- In industry, biotechnology finds use in textile, paper and pulp, food industry, dairy, mining and metal refining.
- Enzymes are biocatalysts which assist various industrial processes.
- Fermentation is the process of metabolism of substrate with the help of enzymes to produce sugars, acids, alcohols, and gases. It finds use in the preparation of ethyl alcohol, vitamins, antibiotics, citric acid, lactic acid, etc.
- Fermentation processes require a medium to which microorganisms can be added. The process is carried out in a fermenter. It can be both aerobic and anaerobic.
- Ethyl alcohol is prepared from molasses and starch by fermentation.
- Acetic acid is prepared by the fermentation of alcoholic solution in the presence of *Mycoderma aceti* bacteria.

Review Questions

1. What is biotechnology? Discuss the application of biotechnology in the following fields:

(a) Agriculture	(b) Medicine
(c) Animal husbandry	(d) Environment
(e) Industrial sector	(f) Energy sector
2. Biotechnology promotes the sustainable development of the environment. Justify the statement.
3. What is a biocatalyst? Discuss its characteristics and applications in various fields.
4. What is fermentation? Explain the general outline of the fermentation process. Also mention the conditions which favour the process of fermentation.

5. Explain the preparation of ethyl alcohol from (a) molasses and (b) starch.
6. How can you prepare acetic acid by fermentation? Explain with the help of a neat labelled diagram.
7. Describe the manufacture of the following by fermentation process:
 - (a) Citric acid
 - (b) Lactic acid
 - (c) Acetone
 - (d) Vitamin B₁₂ (cyanocobalamin)
 - (e) Vitamin B₂ (riboflavin)
 - (f) Vitamin C
 - (g) Penicillin

Multiple Choice Questions

1. The science based on living organisms with widespread application in technology is
 - (a) Bioscience
 - (b) Bioinformatics
 - (c) Biotechnology
 - (d) Bioengineering
2. Biotechnology applied to the medical field is termed as:
 - (a) Green biotechnology
 - (b) Red biotechnology
 - (c) Blue biotechnology
 - (d) White biotechnology
3. Bt cotton, soyabean, rice have been prepared by introducing the protein of bacterium _____ in these plants.
 - (a) *Bacillus thuringiensis*
 - (b) *Bacillus subtilis*
 - (c) *Bacillus licheniformis*
 - (d) *Bacillus megaterium*
4. Common antifungal drugs are
 - (a) Fluconazole
 - (b) Clotrimazole
 - (c) Both of the above
 - (d) None of the above
5. Biodiesel are obtained from:
 - (a) *Jatropha curcas*
 - (b) *Euphorbia*
 - (c) *Calotropis procera*
 - (d) Spirulina, a cyanobacterium.
6. Rhizobium present in the root nodules of leguminous plants convert nitrogen into
 - (a) Ammonia
 - (b) Nitrates
 - (c) Nitrites
 - (d) Ammonium salts
7. Industrial biotechnology is also termed as
 - (a) Green biotechnology
 - (b) Blue biotechnology
 - (c) Red biotechnology
 - (d) White biotechnology
8. Which of the following is incorrect?
 - (a) Amylase converts starch to sugar
 - (b) Proteases assist in the breakdown of proteins

- (c) Lactases break lactose to glucose and galactose
 (d) Trypsin converts sucrose to glucose and fructose
9. Match the enzymes with their industrial applications
- (i) Trypsin a. used for the manufacture of cheese
 (ii) Rennin b. to remove lignin to soften paper
 (iii) Ligninases c. used in detergents to remove fatty and oil stains
 (iv) Lipases d. used to prepare predigested baby food
- (a) (i) a (ii) b (iii) c (iv) d
 (b) (i) d (ii) a (iii) b (iv) c
 (c) (i) d (ii) c (iii) a (iv) b
 (d) (i) c (ii) a (iii) d (iv) b
10. The optimum temperature for the fermentation process is
 (a) 25–35 °C (b) 10–15 °C (c) 30–50 °C (d) 20–40 °C
11. The three by products of the alcohol industry are
 (a) Glycerol, carbon dioxide, oxygen
 (b) Carbon dioxide, acetaldehyde and fusel oil
 (c) Acetic acid, fusel oil, acetaldehyde
 (d) Carbon dioxide, acetaldehyde, acetic acid
12. Rectified spirit is
 (a) 95% alcohol (b) 80% alcohol
 (c) 75% alcohol (d) 100% alcohol
13. The microorganism used for the fermentation of ethyl alcohol to acetic acid is
 (a) Yeast
 (b) *Mycoderma aceti* bacterium
 (c) *Clostridium acetobutylicum*
 (d) *Bacillus thurigiensis*
14. The vitamins that can be obtained by fermentation are
 (a) B₁₂, B₂, C (b) A, B, E (c) A, B, C (d) B, D, K
15. During the manufacture of ethyl alcohol from molasses, the following enzymes assist the fermentation process
 (a) Diastase and maltase (b) Invertase and zymase
 (c) Maltase and zymase (d) Diastase and zymase

Solution

- 1 (c) 2 (b) 3 (a) 4 (c) 5 (a) 6 (b) 7 (d) 8 (d)
 9 (b) 10 (a) 11 (b) 12 (a) 13 (b) 14 (a) 15 (b)

Chapter 25

ANALYTICAL TECHNIQUES IN CHEMISTRY

25.1 Introduction

Analytical chemistry is an important branch that helps in qualitative and quantitative analyses. Qualitative analysis gives information regarding the presence or absence of a component, whereas quantitative analysis addresses the question of how much. Analytical chemistry is an interdisciplinary science that plays a vital role in all streams of chemistry such as organic, inorganic, physical, industrial and biochemistry. It is not only confined to qualitative and quantitative analyses but the advancement of science and development in the field of instrumentation has further quantified its scope. It finds extensive use in environmental science, agricultural science, pollution studies, oceanography, clinical chemistry, medical science, manufacturing industries, biological science, forensic science, and so on.

25.2 Type of Analysis

Three types of analyses can be carried out:

- (a) Physical analysis
- (b) Chemical analysis
- (c) Instrumental analysis

Physical Analysis

The study of physical parameters such as color, smell, physical state, solubility, specific gravity, melting point and boiling point helps in the preliminary investigation of the compound.

The physical properties can be measured by various chemical and instrumental methods, for instance, mass can be estimated by gravimetry, volume by volumetry, electric potential and electric current by conductometry, potentiometry, absorption or emission of radiation by spectroscopy, scattering of radiation by turbidimetry, nephelometry, refraction by refractometry, rotation by polarimetry and optical rotatory dispersion and diffraction by X-ray electron diffraction methods.

These physical and physicochemical methods enable the qualitative and quantitative estimations of the compound.

Chemical Analysis

The qualitative and quantitative estimations of organic and inorganic compounds can be carried out chemically.

Qualitative Estimation of Inorganic Compounds

The qualitative analysis of inorganic compounds is carried out by determining the acid and basic radicals in the compound. For organic compounds, the aromatic and functional groups are determined by the use of specific reagents and compounds.

The quantitative estimation of chemical reactions can be carried out by the following methods of analysis.

- (i) **Gravimetric analysis** In gravimetric analysis, the substance to be estimated is converted into an insoluble precipitate, which is collected, dried and weighed. The process involves several steps in which the sample is prepared, precipitated, filtered, washed, dried and weighed. If the sample is electrolysed and the material deposited at one of the electrodes is weighed, then the process is called electrogravimetry.

The weight of the sample obtained helps in quantitative estimation of the desired substance.

- (ii) **Volumetric analysis** Volumetric analysis is based on measuring the volume of the interacting substances. In this method, a solution of known concentration is prepared with one of the reactants and it is known as the titrant. It is then titrated against the sample solution or unknown solution using a suitable indicator and the end point is determined. The knowledge of end point helps in the quantitative determination of the concentration of the unknown reacting species. This method of volumetric analysis is termed as titration and the common titrations are neutralisation (acid–base) reactions, oxidation–reduction reaction, iodometric and iodimetric titrations, precipitation titrations and complexometric titrations.

- (iii) **Instrumental analysis** Although the physical and chemical methods give fairly good results for the qualitative and quantitative estimations, these days high-quality instrumentation is available that enables estimation with great accuracy and precision. The commonly used analytical techniques are as follows.

1. **Spectrophotometric techniques** These techniques estimate qualitatively as well as quantitatively based on the interaction of electromagnetic waves with matter. These techniques are further classified on the basis of the region of electromagnetic spectrum involved in the interaction, whether there is absorption or emission of radiation and the type of instrument used.

On the basis of the region of electromagnetic spectrum they can be ultraviolet and visible spectroscopy, infrared spectroscopy, NMR spectroscopy, atomic absorption spectroscopy and so on (for details, refer to the chapter on spectroscopy).

2. **Electroanalytical techniques** These techniques make use of the change in electrical properties such as potential difference, conductivity, current, resistance and charge to

measure the chemical properties of the analyte. The various electroanalytical techniques commonly in use are as follows:

- (i) *Potentiometric techniques* These techniques relate the concentration of the reactants and products to the change in potential (for details, refer to Section 25.4).

Other electroanalytical techniques that measure potential or potential difference across the electrodes during the course of the reaction are voltametry and polarography.

pH metry measures the change in pH of the solution with the progress of the reaction (for details, refer to Section 25.5).

- (ii) *Conductometric techniques* In these techniques, the progress of the reaction is followed by conductivity measurements using a conductivity meter. (For details, refer to the chapter on electrochemistry, Section 16.6).

- (iii) *Coulometric techniques* These techniques analyse the amount of analyte oxidised or reduced on passing a definite quantity of current. The coulometric method of analysis is based on the Faraday's law of electrolysis, according to which the extent of chemical reaction at an electrode is directly proportional to the quantity of electricity passing through the electrode.

If the technique measures the current passing through the cell with the progress of the reaction then it is termed as amperometry.

The various instrumental methods are summarised in Table 25.1.

Table 25.1 Classification of instrumental methods of analysis

S.No	Method	Principle	Property measured
1	Electroanalysis methods	Changes in the electrical properties of the system	Mass of deposited substance
	Electrogravimetry	Electrolysis is carried out	Material deposited on one of the electrode is weighed
	Coulometry	Deposition of matter on an electrode during electrolysis	Quantity of electricity and time
	Conductometry	Change in electrical conductivity of a solution during chemical reaction	Electrical conductivity, electrical resistance
	Amperometry	Potential applied between the indicator electrode and depolarised reference electrode is kept constant	Current through the electrolytic cell is measured
	Potentiometry	Change in electrode potential of a system during chemical reaction	Electrode potential
	Polarography	Electrode polarisation	Voltage, current
2	Spectroscopic methods	Interaction of matter with electromagnetic radiation	Radiant energy of a particular wavelength
	Atomic absorption spectroscopy	Atomising specimen	Absorption of radiation

	Absorption spectrophotometry (colorimetry, photoelectron colorimetry)	Absorption of poly- and monochromatic radiant energy by molecules and ions in solution	Optical density of the solution
	Emission spectroscopy	Sample is subjected to an electric arc or spark plasma. Emission of radiation	Position and intensity of spectral lines
	Turbidimetry	Absorption and scattering of light beam by turbid media	Amount of light stopped or scattered by a suspension
	Nephelometry	Reflection and scattering of light beam by colloidal solution	Amount of light stopped or scattered by a suspension
	Refractometry	Refraction of light by matter	Refractive index
3	Nuclear magnetic resonance	Nuclear magnetism (resonance absorption of electromagnetic radiation by matter in magnetic field)	Position and intensity of lines of NMR spectrum
4	Radiometric methods	Conversion of stable isotopes of an element to radio isotopes	Intensity of radiation. Induced radioactivity
	Isotope dilution	Change in specific activity of the compounds labeled with a radioisotope	Radioactivity
5	Kinetic methods	Speed of chemical reaction may be increased by the addition of a catalyst	Change in the absorbance of solution for visible or UV radiation

25.3 Separation Techniques

Separation is the process of parting or dividing a homogenous mixture or mass into individual components, units or even elements. Many methods are employed for the separation process. Separation is used for purification, qualitative identification and quantitative determination. Some important techniques are as follows.

Chromatography

Chromatography is a technique widely used for the separation and purification of organic and inorganic substances. It consists of a fixed phase known as the stationary phase and a moving phase termed as the mobile phase. The stationary phase may be a solid or a liquid adsorbed on a solid support. The mobile phase may be a volatile liquid or a gas. The mixture to be separated or purified is loaded on the stationary phase and the mobile phase is run on it. The mixture migrates with the mobile phase and the different components are separated by the differential migration and adsorption of the components. The individual components are then separated and extracted by separate techniques. Depending upon the stationary and the mobile phases, chromatographic techniques can be of various types such as those shown in Table 25.2.

Table 25.2 Types of chromatographic techniques

Phase type	Name of the process	Phase of the sample	Second phase
Solid liquid	Adsorption chromatography	Solution	Solid absorbent
	Thin-layer chromatography	Solution	Fine powder supported on a glass plate
	Ion exchange chromatography	Solution	Ion exchange resin
Liquid–liquid	Partition chromatography	Solution	Immiscible solvent on a solid matrix
	Paper chromatography	Solution	Immiscible solvent adsorbed on paper matrix
	Thin-layer chromatography	Solution	Immiscible solvent absorbed on fine powder supported on a glass plate
Liquid–gas	Gas–liquid chromatography	Gas	Condensed liquid or solvent held on a solid matrix
Gas–solid	Gas–solid chromatography	Gas	Solid adsorbent

25.4 Potentiometry

As is well known that the potential of an electrolyte can be determined by dipping an electrode into the electrolyte solution. The electrode potential depends upon the nature of the electrolyte and the concentration or activity of the ion with which it is in equilibrium. Just as conductivity values are used to detect end points in various titrations (refer to electrochemistry, Section 16.6 on conductometric titrations), similarly the measurement of potential with an appropriate indicator electrode in conjunction with a reference electrode can be used to find the end point in various titrations. The potential changes with the change in concentration of the solution being titrated and near the end point there is a sharp change in the potential of the indicator electrode.

In potentiometric titrations, the potential of the cell is given by the sum of the potentials of indicator electrode, reference electrode and the liquid junction.

$$E_{\text{cell}} = E_{\text{reference}} + E_{\text{indicator}} + E_{\text{junction}}$$

Calomel electrode is generally used as the reference electrode, and the choice of indicator electrode depends upon the type of titration and the titrant used. In these titrations, the course of titration is followed by measuring the concentration of one or more species potentiometrically.

The change in the electrode potential is noted upon the addition of the titrants. At the end point, the rate of change of the potential is the maximum. A curve of potential versus the volume of the titrant helps in detecting the end point. Potentiometric titrations are applied to all types of chemical reactions.

Instrumentation

The measurement is generally carried out with the help of a potentiometer. In this method an unknown cell EMF to be measured is compared with a known EMF source. The principle of a simple potentiometer is outlined in Figure 25.1. In this apparatus a battery B consists of two dry cells in series and supplies current. R is a variable resistance and V is a voltmeter. A galvanometer

G of intermediate sensitivity is connected to a resistor R_D in parallel. The reference and indicator electrodes are connected by a reversing switch. To measure the potential, the electrodes are dipped in sample solution, S_1 is closed and R is adjusted till the galvanometer does not show deflection (null point). If null point is not obtained, S_2 is reversed and the process is repeated after each addition of the reagent.

Automatic self-balancing null-type potentiometric recorders are available for the purpose.

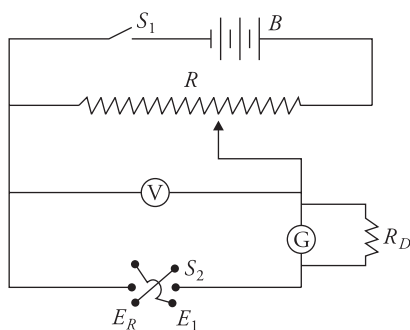


Figure 25.1 Principle of a potentiometer

1. Potentiometric Titrations

Potentiometric titrations are used to determine the end point in various acid–base titrations, redox titrations, precipitation titrations, complexation equilibria, etc.

- (a) *Acid–Base Titrations* For these titrations, generally hydrogen electrode is used in conjunction with N-calomel electrode as a reference electrode. A known volume of acid to be titrated is taken in a beaker having an automatic stirrer. Hydrogen and calomel electrodes are dipped inside the beaker and the electrodes are connected to the potentiometer that records the EMF of the solution. The base is added gradually from the burette into the beaker and the EMF is measured after each addition of the base. The values of EMF are plotted against the volume of base added and a curve as shown in Figure 25.2 is obtained.

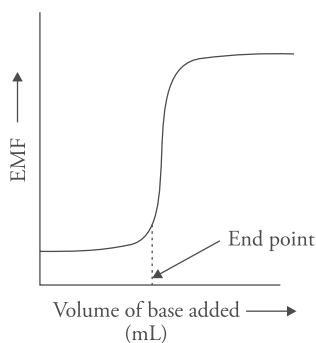


Figure 25.2 Plot of EMF against volume of base added

The potential of hydrogen electrodes is given by

$$E = E^0 - 0.0591 \log a_{\text{H}^+} \text{ at } 25^\circ\text{C}$$

where E^0 is the standard electrode potential

$$\text{or } E = E^0 + 0.0591 \text{ pH } (\because \text{pH} = -\log a_{\text{H}^+}).$$

Hence, it can be concluded that the change in EMF or electrode potential is proportional to the change in pH during titration. The end point is given by the point where the EMF increases rapidly.

The end point can be located exactly by a differential plot in which the slope of the curve, that is, $\Delta E/\Delta V$, is plotted against the volume of alkali added (V). The value of $\Delta E/\Delta V$ is maximum at the end point (Fig. 25.3).

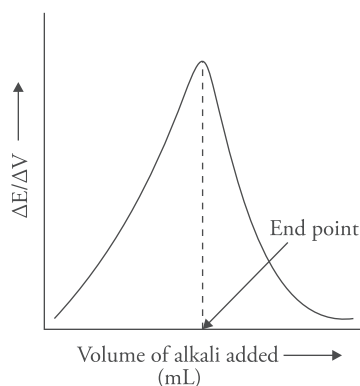


Figure 25.3 Plot of $\Delta E/\Delta V$ against the volume of alkali added

- (b) *Oxidation–Reduction Titrations* The method of carrying out oxidation reduction titration potentiometrically is similar to that of neutralisation titration except that the indicator electrode is an inert electrode such as platinum wire. The potential is proportional to the logarithm of the concentration ratio of the two oxidation states of the substances being oxidised or reduced. The titration involves transfer of electrons. For example,



The acidic ferrous solution is taken in the beaker and the standard ceric solution is added gradually from the burette. The EMF is obtained after every addition of the titrant from the burette. The potential is plotted against volume of titrant added, and the end point is obtained graphically. A differential plot can be drawn by plotting $\Delta E/\Delta V$ against volume (V). The maximum value of $\Delta E/\Delta V$ gives the end point as in the neutralisation titration.

Advantages of potentiometric titrations

1. They can be used for dark-colored solutions where ordinary titration with indicator fails.
2. The method helps to analyse dilute solutions with high degree of accuracy.
3. The method is inexpensive, reliable, readily available and very accurate.
4. Interpretation of titration curve is very easy.

25.5 pH metry

pH metry involves the measurement of pH with the addition of the reactants. Similar to potentiometric titrations, the change in pH is noted with the addition of reagent from the burette and the end point can be determined graphically by plotting the pH against the volume of the titrant added.

The pH is measured with the help of pH meter that measures the potential difference (in mV) between the electrodes and converts it to a pH display. A combined glass electrode (calomel electrode and glass electrode) is used for pH measurements (refer to the chapter on electrochemistry). The combined electrode is dipped in the solution under study and pH is read directly from the digital display of the pH meter.

Standardisation of pH meter

For standardisation, the pH electrode is connected to the socket of the pH meter. The electrode is dipped in distilled water and the instrument is connected to the mains supply and warmed up for 10–15 min. After the warm up, the instrument is calibrated with the help of solutions of known pH (pH 4, 7 and 9.2).

The steps involved in the calibration are as follows:

- The electrode is dipped in buffer solution of pH 7.
- The temperature is set according to the temperature of buffer solution.
- The function selector knob is set to pH position and the pH of the solution is adjusted to 7 with the help of 'CALIBRATE' control knob.
- The selector switch is moved to 'standby' mode.
- The electrode is washed with distilled water, dried with tissue paper and dipped in the buffer solution of pH 4 or 9.2.
- The function selector switch is moved to pH position and the 'SLOPE' is adjusted until the digital display shows exactly 4 or 9.2 as the case may be.
- The instrument is now calibrated and ready to read the pH of any solution.

Buffer solutions

A buffer is a solution whose pH does not vary with the addition of small quantities of acid or base. Buffer solutions are used to standardise the pH meter.

These days, buffer tablets are commercially available. Buffer tablets of pH 4, 7 and 9.2 are commonly available, and a tablet dissolved in 100 mL of distilled water gives the solution of the required pH.

Buffers can also be prepared by mixing suitable acid or base with their salts (Tables 25.3 and 25.4).

Table 25.3 pH of some buffer solutions

Buffer solution	pH
0.01 M CH_3COOH + 0.01 M CH_3COONa	4.70
0.01 M NaH_2PO_4 + 0.01 M H_3PO_4	6.85
0.05 M Borax + 0.05 M tetra boric acid	9.18
0.025 M NaHCO_3 + 0.025 M Na_2CO_3	10.00

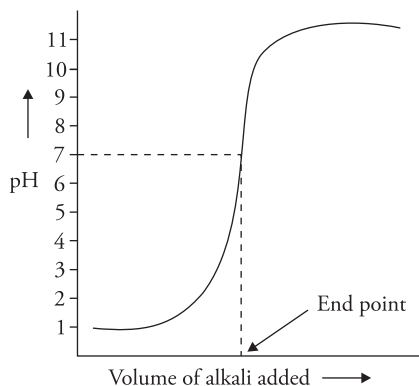
Table 25.4 Commonly used buffer mixtures

Mixture	Composition	pH
Formate buffer	Formic acid (HCOOH) + sodium formate (HCOONa)	3.7
Benzoate buffer	Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) + sodium benzoate ($\text{C}_6\text{H}_5\text{COONa}$)	4.2
Acetate buffer	Acetic acid (CH_3COOH) + sodium acetate (CH_3COONa)	4.7
Phosphate buffer	Sodium hydrogen phosphate (NaH_2PO_4) + disodium hydrogen phosphate (Na_2HPO_4)	6.8
Ammonia buffer	Ammonium hydroxide (NH_4OH) + ammonium chloride (NH_4Cl)	9.2

pH metric titrations

Titration of strong acid versus strong base

The acid to be titrated is taken in a beaker. The combined glass electrode connected to the pH meter is dipped in the beaker and the pH is noted. Strong base is filled in the burette and is added gradually to this solution with constant stirring and the pH is obtained after each addition. The pH is then plotted against the volume of the base added. The volume at pH 7 (neutral) gives the end point of the titration.



Advantages of pH metry:

The method gives accurate results for end point without the use of indicator and eliminates errors because of difference in the observation of color changes of the indicator at the end point.

Summary

- Analytical chemistry helps in the quantitative and qualitative analyses of substances.
- Three types of analyses are carried out: physical, chemical and instrumental.
- Physical analysis involves the study of physical parameters such as color, smell, solubility, specific gravity, melting point and boiling point.
- Chemical analysis: It can be qualitative and quantitative.
- Qualitative analysis addresses the issue of what type. The qualitative analysis of organic and inorganic compounds can be carried out by using specific reagents called group reagents, which help in identifying those compounds.
- Quantitative analysis is carried out either by precipitating the substances and measuring their masses – which is called gravimetry – or by measuring the volume of the reacting substances, which is called titrimetry methods.
- Instrumental analysis involves the use of advanced and sophisticated instruments for estimating the compounds both qualitatively and quantitatively. These include various spectroscopic techniques such as absorption and emission spectroscopy, UV–visible spectroscopy, infrared spectroscopy, NMR spectroscopy, etc. The electroanalytical techniques used for estimation are potentiometric methods, conductometric methods, pH metric methods, coulometry, amperometry, voltammetry, polarography, etc.
- Chromatography is a process of separating and purifying organic and inorganic compounds by the use of a stationary phase and a mobile phase.

Review Questions

1. What are the different types of analysis carried out to estimate the substances qualitatively and quantitatively?
2. Discuss the classical methods used in quantitative estimation of chemical compounds.
3. What is the advantage of instrumental methods over classical methods of analysis? Explain in brief various instrumental methods used for the analysis of chemical substances.
4. What is chromatography? Explain the underlying principle.
5. What is potentiometry? Explain the instrumentation. Explain how potentiometric methods help to determine the end point in the following

- (i) Acid–base titrations
 - (ii) Oxidation–reduction titrations.
6. What is pH metry? How is a pH meter standardised? Explain the determination of end point in acid–base titrations using a pH meter.

Multiple Choice Questions

1. The branch of chemistry that deals with the qualitative and quantitative estimations is
 - (a) Analytical chemistry
 - (b) Biochemistry
 - (c) Nanochemistry
 - (d) Quantum chemistry
2. Which among the following methods gives the most accurate and precise results in analysis
 - (a) Physical methods
 - (b) Chemical methods
 - (c) Instrumental methods
 - (d) None of the above
3. The classical methods for the quantitative estimation of substances are
 - (a) Gravimetric methods
 - (b) Volumetric methods
 - (c) Both the above
 - (d) None of the above
4. The analytical technique based on the interaction of electromagnetic radiation with matter is
 - (a) Spectrophotometry
 - (b) Conductometry
 - (c) Amperometry
 - (d) Turbidimetry
5. The method that studies the change in conductivity of the solution during chemical reaction is
 - (a) Voltammetry
 - (b) Conductometry
 - (c) Amperometry
 - (d) Potentiometry
6. Potentiometric titrations are based on the measurement of
 - (a) Quantity of electricity and time
 - (b) Electrical conductivity and resistance
 - (c) Electrode potential
 - (d) Absorption of radiation
7. The amount of light stopped or scattered by a suspension is measured in
 - (a) Turbidimetry
 - (b) Nephelometry
 - (c) Both the above
 - (d) None of the above
8. An important technique employed for the separation and purification of compounds is
 - (a) Chromatography
 - (b) Conductometry
 - (c) Potentiometry
 - (d) Coulometry

Solution

- 1 (a) 2 (c) 3 (c) 4 (a) 5 (b) 6 (c) 7 (c) 8 (a)

Chapter 26

CHEMISTRY OF CARBON AND HYDROGEN

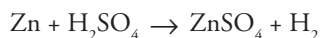
26.1 Hydrogen

Hydrogen is the first element of the periodic table with the electronic configuration $1s^1$. Its position in the periodic table is anomalous. It resembles both alkali metals and halogens. Similar to alkali metals, it has just one electron in its valence shell and has a tendency to lose electron and form H^+ ion. It resembles halogen (group 17) as both are one electron short of the noble gas structure. Although hydrogen does not normally form a negative ion, it does form ionic hydrides M^+H^- (e.g., LiH and CaH_2) with highly electropositive elements. Hydrogen also has resemblance with elements of group 14, as both have half-filled valence shell.

26.2 Preparation of Hydrogen

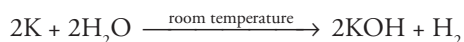
Laboratory preparation

- (i) **By the action of acids on metals** In the laboratory, hydrogen is prepared by the action of dilute H_2SO_4 on granulated zinc.

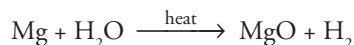


The evolved gas is collected by the downward displacement of water taking utmost care to remove all the air from the apparatus as hydrogen forms an explosive mixture with air.

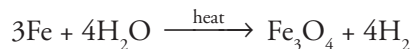
- (ii) **By the action of water on metals** Active metals such as Na, K and Ca react with water at room temperature.



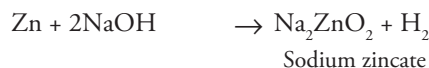
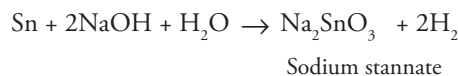
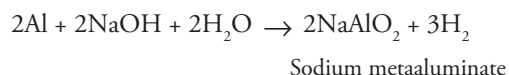
Metals such as Zn, Mg and Al react with water on heating



Iron and nickel react with steam to liberate hydrogen gas



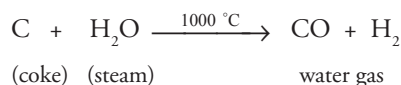
- (iii) **By the action of alkalis on metals** Hydrogen gas is formed by the action of alkalis on metals such as zinc, tin and aluminium.



26.3 Industrial Method of Preparation of Hydrogen

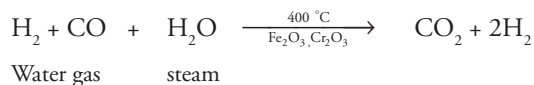
On a large scale, hydrogen gas can be prepared by the following methods.

- (i) *By passing steam over red-hot coke* When steam is passed over red-hot coke at 1000 °C, a mixture of carbon monoxide and hydrogen (water gas) is formed



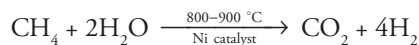
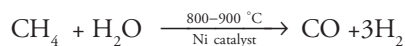
Pure hydrogen cannot be obtained from water gas, as it is difficult to remove CO. Carbon monoxide can be removed either by

- Liquefying it at low temperature and under pressure
- Mixing the gaseous mixture (water gas with more steam and passing it over a mixture of ferric oxide (Fe_2O_3) and chromium oxide (Cr_2O_3) at 400 °C. This is called Bosch process.



Carbon dioxide is removed by dissolving in water under pressure (25 atm) or by reacting with K_2CO_3 solution forming KHCO_3 and pure hydrogen gas.

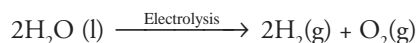
- (ii) *Steam-reforming process* Hydrocarbons such as methane are mixed with steam and passed over a nickel catalyst at 800–900 °C.



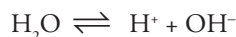
The gas emerging from the reformer is a mixture of CO, CO₂, H₂ and excess of steam. To obtain pure hydrogen, this mixture is mixed with more steam in the presence of iron/copper catalyst at 400 °C. The CO converts to CO₂, which is removed either by dissolving in water under pressure or by absorbing on K₂CO₃.



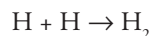
- (iii) *Electrolysis of water* Hydrogen gas of high purity can be prepared by the electrolysis of water in the presence of small amount of acid or base.



Hydrogen gets collected at the cathode and oxygen is liberated at the anode



At the cathode $\text{H}^+ + \text{e}^- \rightarrow \text{H}$



At the anode, $4\text{OH}^- - 4\text{e}^- \rightarrow 4\text{OH}$



A better and more economic way of splitting water is by the use of solar energy. Semiconductor electrodes such as titanium oxide (rutile anode) and platinum counter electrodes (cathode) are used for the solar splitting of water (for details, refer to Section 18.10).

26.4 Properties of Hydrogen

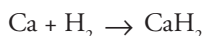
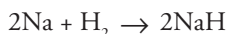
Physical properties

- It is a colorless, odorless, tasteless, diatomic gas that is lighter than air.
- The density ratio of hydrogen and air is 0.0695:1.

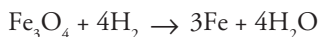
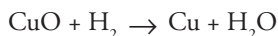
- It is sparingly soluble in water with a melting point of $-253\text{ }^{\circ}\text{C}$ and boiling point $-259\text{ }^{\circ}\text{C}$ at one atmospheric pressure.
- It gets adsorbed on the surface of metals such as Pt, Pd and Au. The process is termed as occlusion of hydrogen.

Chemical properties

1. *Reaction with non-metals* It reacts with non-metals such as O, S, N and Cl to form covalent compounds such as H_2O , NH_3 and HCl .
2. *Reaction with metals* Metals react with hydrogen to form hydrides.



3. *Reducing nature* Hydrogen is a reducing agent and reduces the oxides of less electronegative metals such as Cu, Zn, Pb and Fe.



26.5 Isotopes of Hydrogen

There are three isotopes of hydrogen namely protium (H), deuterium (D) and tritium (T). Each of these three isotopes of hydrogen has one proton and one electron; however, the number of neutrons is different. Protium or light hydrogen is the commonest isotope of hydrogen with no neutron. Deuterium or heavy hydrogen has one neutron, whereas tritium an unstable radioactive isotope of hydrogen contains two neutrons in its nucleus. As the percentage difference in the masses of the three isotopes of hydrogen is more than any other isotopes, there is a marked difference in their physical properties.

The common physical properties of H_2 , D_2 and T_2 are given in Table 26.1.

Table 26.1 Common physical properties of H_2 , D_2 and T_2

Property	H_2	D_2	T_2
Mass of atom (amu)	1.0078	2.0141	3.0160
Freezing point ($^{\circ}\text{C}$)	-259.0	-254.3	-252.4
Boiling point ($^{\circ}\text{C}$)	-252.6	-249.3	-248.0
Heat of fusion (kJ mol^{-1})	0.117	0.197	0.250
Heat of vaporisation (kJ mol^{-1})	0.904	1.226	1.393
Bond energy (kJ mol^{-1})	435.9	443.4	446.9

26.6 Storage of Hydrogen

Hydrogen has high calorific value (three times greater than gasoline) but it is highly flammable and forms an explosive mixture with air; hence, its storage and transportation is one of the most challenging task.

The methods employed for the storage of hydrogen are as follows:

1. Physical storage

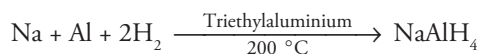
- (a) Hydrogen is compressed to its liquid state at high pressure in high-pressure tanks.
- (b) Hydrogen can be cooled to $-253\text{ }^{\circ}\text{C}$ at a pressure of 6–350 bar to give cryogenic hydrogen.
- (c) Many molecules reversibly adsorb hydrogen in their structure.

The commonly used substances for hydrogen storage are as follows

- Carbon nanotubes and carbon bucky balls store hydrogen in the spaces in between and inside.
- Carbon materials such as graphene store hydrogen easily and release it on heating up to $450\text{ }^{\circ}\text{C}$.
- Another class of synthetic porous materials that adsorb and store hydrogen is metal–organic frameworks (MOFs). Hydrogen gas is stored in the spaces between these molecules and can be recovered for further use by raising the temperature.
- As clathrate hydrates: In clathrates, the atoms or molecules are trapped inside the cavities of atoms, molecules or crystal lattice of other compounds without bond formation. Hydrate clathrate is used to store hydrogen, although high pressure is required to stabilise the compound.

2. Chemical storage

- *As hydrides* In chemical storage, hydrogen is stored as hydrides. The most commonly used substance for chemical storage of hydrogen is sodium aluminium hydride or sodium alanate, which is an inorganic compound with the formula NaAlH_4 . It serves as an important agent for the reversible storage of hydrogen. Hydrogen is stored by reacting with sodium and aluminium at high pressure and temperature of about $200\text{ }^{\circ}\text{C}$ in the presence of triethylaluminium catalyst.



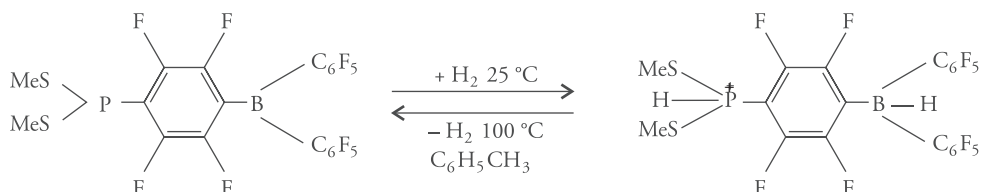
When heated to above $200\text{ }^{\circ}\text{C}$, sodium tetrahydroaluminate releases about 7.4% hydrogen by weight.



The release of hydrogen is catalysed by titanium.

Other metal hydrides used to store hydrogen are MgH_2 , LiAlH_4 , LiH , TiFeH_2 , palladium hydride, ammonia borane, etc.

- **Carbohydrates** Glucose molecules also release hydrogen. On being treated in a bioreformer in the presence of enzymes, it is believed that nearly 12 moles of hydrogen are released per glucose molecule.
- **Ammonia** In the presence of a suitable catalyst ammonia also releases hydrogen, and hence can be used to store hydrogen.
- **Amine borane complexes** Other hydrogen carriers are amine borane complexes such as ammonia borane. When amine borane is ignited it yields boron nitride and hydrogen gas.
- **Formic acid** Formic acid has also been used as a material to store hydrogen. It stores about 4.3 weight percent of hydrogen, which can be decomposed to produce H_2 and CO_2 in aqueous solution in the presence of a suitable catalyst.
- **Storage materials based on imidazolium ionic liquids** These can add hydrogen atom reversibly and can store about 30 g/L of hydrogen at atmospheric pressure. For example, phosphinoborane accepts hydrogen at 25 °C and one atmosphere pressure, which is expelled on heating to 100 °C.



26.7 Compounds of Hydrogen

Hydrides

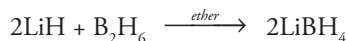
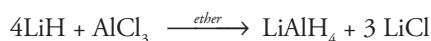
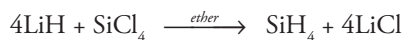
Hydrides are the binary compounds of elements with hydrogen. Hydrides are divided into four classes:

1. Ionic hydrides or salt-like hydrides
 2. Covalent hydrides or molecular hydrides
 3. Metallic hydrides or interstitial hydrides
 4. Polymer hydrides.
1. **Ionic hydrides** They are salt-like hydrides and are also termed as saline hydrides. Elements having electronegativities between 0.9 and 1.2 (i.e., group 1, group 2 and lanthanoids) form ionic hydrides by the direct combination with hydrogen.

Preparation They are prepared by heating alkali and alkaline earth metals directly with hydrogen. The reactivity of the alkali metals toward hydrogen increases from Li to Cs. For example, lithium requires a temperature of 600 °C to form LiH, whereas NaH can be formed at 300 °C.

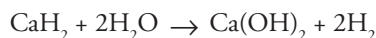
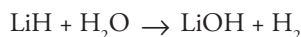
Properties

- They are solids with high melting points.
- The ionic character of hydrides increases from Li to Cs.
- The chemical reactivity of the hydrides increases from LiH to CsH and from CaH₂ to BaH₂. Hydrides of group 1 are more reactive than those of group 2.
- The stability of the hydrides decreases from Li to Cs.
- The reducing power of metal hydrides increases down the group.
 - (i) Lithium hydride exhibits slight covalent character and is soluble, to a small extent, in ether and other polar solvents. Few important reactions are as follows:

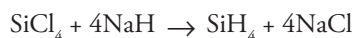
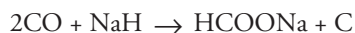


- (ii) Lithium hydride reacts with nitrogen at high temperature to form LiNH₂, Li₂NH or Li₃N.

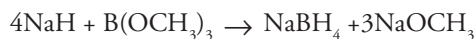
- All ionic hydrides react with water to liberate hydrogen.



- They are powerful reducing agents



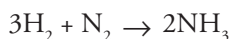
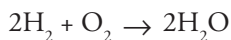
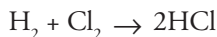
- Sodium hydride is also a strong reducing agent. It finds extensive use as a reducing agent as NaBH₄.



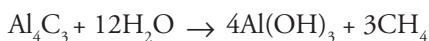
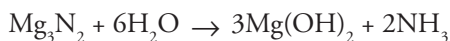
- 2. Covalent hydrides or molecular hydrides** p block elements combine with hydrogen to form covalent hydrides. Except boron, covalent hydrides are represented by XH_n or XH_{8-n} , where n is the group number to which X belongs.

Preparation

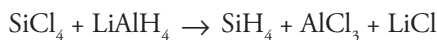
- (i) By direct combination of elements (H_2O , NH_3 , HCl and HF)



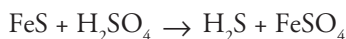
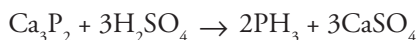
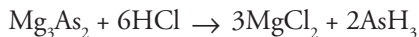
- (ii) By the hydrolysis of metal borides, carbides, nitrides, phosphides, etc.



- (iii) Reduction of halide with LiAlH_4 in a dry solvent such as ether.



- (iv) By treating an appropriate binary compound with an acid.



Properties

- They have low melting and boiling points and are generally volatile. Hydrides with higher molecular weight are liquids with low volatility.
- They are present in molecular forms in all the three states.
- They decompose on heating and their stability decreases down the group.

- 3. Metallic or interstitial hydrides** Metallic hydrides are formed by transition metals (d block elements) with electronegativity values between 1.2 and 1.4. They are also called interstitial hydrides because hydrogen is absorbed and retained in the interstices of the metal.

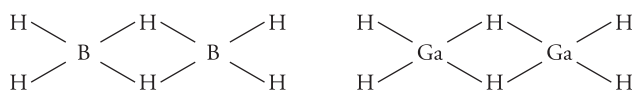
Preparation

- (i) By heating the metal with hydrogen at high pressure.

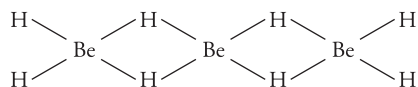
Properties

- They are interstitial compounds with non-stoichiometric composition ($\text{PdH}_{0.7}$, $\text{LaH}_{2.87}$, $\text{ZrH}_{1.9}$, $\text{VH}_{1.6}$, etc.).
 - Owing to the presence of atomic hydrogen they act as powerful reducing agents.
 - They show resemblance in properties to their parent metal, that is, they are hard, have metallic luster and conduct electricity; however, they are less dense than the parent metal.
4. **Polymeric hydrides** A polymeric hydride is one in which two or more atoms of an element are linked through hydrogen. Such types of hydrides are generally formed by elements such as Be, Mg, B, Al and Ga.

Polymeric Be and Mg hydrides are formed by reducing beryllium and magnesium chloride with lithium hydride. In these compounds, hydrogen forms a bridge bond.



Gallium hydride is a dimer-like boron hydride



These hydrides are unstable solids, non-conductors and are powerful reducing agents.

Important hydrides

Hydrocarbons They are the hydrides of carbon. Carbon forms a wide variety of hydrides that form the basis of organic chemistry. The important hydrides of carbon are as follows:

1. Alkanes (paraffin's) – $\text{C}_n\text{H}_{2n+2}$
2. Alkenes (olefins) – C_nH_{2n}
3. Alkynes (acetylenes) – $\text{C}_n\text{H}_{2n-2}$
4. Aromatic compounds

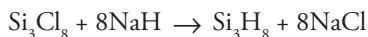
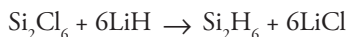
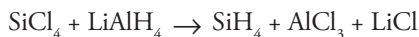
The details are beyond the scope of the present text.

Silanes and Germanes

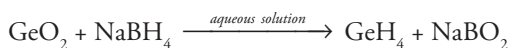
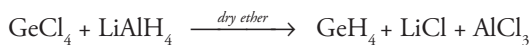
They are hydrides of silicon and germanium with the general formula $\text{Si}_n\text{H}_{2n+2}$ and $\text{Ge}_n\text{H}_{2n+2}$ respectively. They may be straight-chained or branched and are rarely ringed, and no hydrides with multiple bonds have been reported. Silanes upto Si_6H_{14} are known, although only monosilane SiH_4 is of importance. Germanes are characterised upto $n = 5$ for example Ge_5H_{12} .

Preparation

On reduction of SiCl_4 with LiAlH_4 , LiH or NaH in ether solution at low temperature yields monosilane SiH_4 .

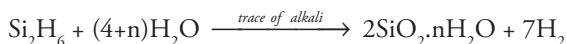


Germanes are also prepared by reducing GeCl_4 or GeO_2 with LiAlH_4 or NaBH_4 in dry ether or aqueous solution

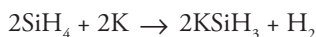


Properties

Silanes are more reactive than alkanes. They are spontaneously inflammable and decompose by moderately strong acids and bases. They react with hydrogen halides at 100–125 °C in the presence of aluminium halides as catalysts to give halosilanes.



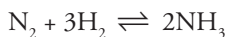
They react with potassium in glyme(1,2-dimethoxyethane) at –78 °C.



Germanes are volatile liquids or colorless gases. They are less volatile, less flammable than silanes and are unaffected by water or aqueous acids or alkalis. Germanes oxidise less readily. GeH_4 reacts with oxygen at an elevated temperature of about 170 °C and Ge_2H_4 at about 100 °C. Germanes are less reducing than silanes.

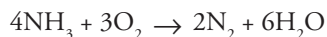
Ammonia NH_3

It is a hydride of nitrogen formed by the direct reaction of nitrogen with hydrogen at 200 atmospheric pressure in the presence of finely divided iron with little molybdenum at 500 °C.

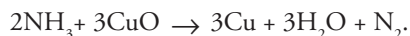


Properties

It is a colorless gas with a pungent odor. It is readily soluble in water and is basic in nature. It burns in air to form nitrogen.



Similarly, on passing over red-hot copper, it is oxidised to nitrogen.



Uses

It finds use in the manufacture of nitric acid, fertilisers, urea, etc.

26.8 Applications of Hydrogen

Hydrogen finds extensive applications in a number of fields

- It is used in the manufacture of ammonia by Haber's process.
- It is used to fill balloons because of its low density.
- It is used in the manufacture of methanol and in the hydrogenation process. It finds extensive use in the preparation of vanaspati ghee from vegetable oils. It is also used as a reducing agent.
- It finds use in the manufacture of ammonia, which is subsequently used for making fertilisers.
- Oxyhydrogen flames are used in welding and other allied activities.
- Hydrogen is a very promising fuel for the future as its calorific value is high, it is renewable (can be provided by electrolysis of water) and does not produce pollutants on burning. It can be used similarly as natural gas. Liquid hydrogen is used as a fuel in jet aircraft and it is also used in fuel cell devices that combine hydrogen and oxygen to produce electricity (for details, refer to Section 16.18).

26.9 Carbon

Carbon is widely distributed in nature and is an essential constituent of all living matter. It occurs in both free state and in combined form. In free state it is available in the form of diamond, graphite and coal, whereas in combined state it appears as carbondioxide in the atmosphere, as hydrocarbons in natural gas, petroleum, etc, and as carbonates and minerals in the earth's crust. Besides the earth's crust, carbon is also found in the sun, in meteorites and in the universe.

With an atomic number of six it finds place in group 14 of the periodic table and has an electronic configuration of $[\text{He}] 2s^2 2p^2$.

26.10 Isotopes

Although about 15 isotopes of carbon are known, the three common and naturally occurring isotopes of carbon are ^{12}C , ^{13}C and ^{14}C . ^{12}C and ^{13}C are stable, whereas ^{14}C is radioactive with

a half life of 5700 years. Radiocarbon ^{14}C contains six protons and eight neutrons. The relative natural abundance of the three isotopes is as follows: $^{12}\text{C} = 98.89\%$, $^{13}\text{C} = 1.11\%$, $^{14}\text{C} \sim 10^{-12}$. ^{12}C is the most abundantly available isotope that is found in the living system and in the earth's atmosphere. ^{13}C finds its use in various chemical studies, for reaction rate determination and for finding out the mechanism of various reactions, spectroscopic studies, etc. ^{14}C finds extensive use in the determination of age of objects by radio carbon dating. It decays into ^{14}N through beta decay.

26.11 Allotropes of Carbon

Carbon shows allotropy and occurs in a number of forms having different physical but the same chemical properties.

Diamond and graphite are the crystalline forms of carbon, whereas wood, charcoal, coke, animal charcoal and lampblack are its amorphous forms. A new form of carbon, buckminster fullerene C_{60} , is also known.

Graphite and fullerene have been discussed in detail in the chapter on solid state (Sections 11.18 and 11.17, respectively), and coal and coke in the chapter on fuels (Sections 1.6–1.8). Let us here discuss the structure and properties of diamond.

Diamond

It is crystalline and is the hardest substance known. It is the purest and densest form of carbon with a specific gravity of 3.5. It is a bad conductor of electricity and has a high refractive index 2.45, which makes it valuable as a gem. Pure diamond is colorless and transparent to X-rays.

The carbon atom in diamond is sp^3 hybridised, and each carbon atom is strongly bonded to four neighboring atoms, which are situated at the corners of a regular tetrahedron. All the atoms in the diamond crystal are bound by strong covalent bonds, as the C–C bonds in diamond are very strong and thus it is very hard.

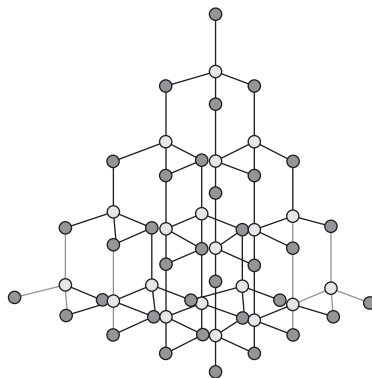
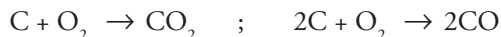


Figure 26.1 Structure of diamond

26.12 Chemical Properties of Carbon

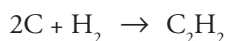
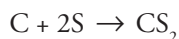
(i) *Combustion*

It burns in excess of air or oxygen to produce carbondioxide, whereas in limited supply of air carbon monoxide is formed.



(ii) *Combination with elements*

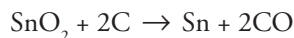
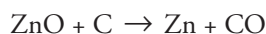
At high temperature it combines with sulphur to form carbon disulphide and it combines with hydrogen in the presence of an electric arc to form acetylene.



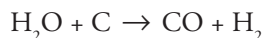
(iii) *Reducing action*

Carbon is a good reducing agent; it reduces

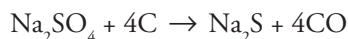
- (a) Metallic oxides to metals.



- (b) Steam to hydrogen.



- (c) Sulphates to sulphides.

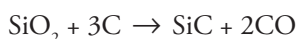
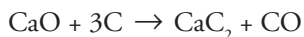


- (d) Sulphuric acid to sulphur dioxide and nitric acid to nitrogen peroxide.



(iv) *Formation of carbides*

Calcium oxide and silica react with carbon in an electric furnace to form calcium carbide and silicon carbide, respectively



26.13 Uses

- Carbon is an important constituent of all living matter as proteins, carbohydrates and fats.
- As graphite it finds its use in making lead pencils, as a lubricant either in dry form or as a suspension in oils, for making electrodes, crucibles, for producing a conducting surface on non-conductors before electroplating.
- As coal and coke it is used as a fuel in metallurgical operations.
- As charcoal it is used for absorbing coloring matter from liquids and is also used in the sugar industry.
- As lampblack it finds extensive use in the manufacture of printing inks, black paints and boot polishes.
- As diamond it is a precious gem used for making jewellery. Black diamond or carbonados are of no value as gems and find use as abrasives for cutting and polishing.

Summary

- Hydrogen is the first element of the periodic table and appears in group I, carbon finds place in group 14 of the periodic table.
- Hydrogen can be prepared by the action of water, acids and alkalis on metals. Industrially, it is prepared by passing steam over red-hot coke (Bosch process), steam reforming (mixture of hydrocarbons and steam are passed over nickel catalyst at 800–900 °C) or by the electrolysis of water.
- The three isotopes of hydrogen are protium ^1H , deuterium ^2H and tritium ^3H .
- Hydrides are important compounds of hydrogen. They can be
 - (a) Ionic or salt like, such as NaH .
 - (b) Covalent or molecular, such as HCl , NH_3 , SiH_4
 - (c) Metallic or interstitial, such as $\text{PdH}_{0.7}$, $\text{LaH}_{2.87}$
 - (d) Polymeric, such as boron hydrides
- Hydrogen is a very useful fuel but its storage and transportation is a challenging task. It can be stored either physically or chemically.
- Hydrogen is stored physically by liquefaction under high pressure, cooling at low temperature (cryogenic hydrogen), carbon nanotubes or carbon bucky balls porous materials such as metal organic frameworks (MOF's) also adsorb and store it. Hydrogen is retrieved from them by raising the temperature.
- Hydrogen can be stored chemically as sodium alanates (NaAlH_4), MgH_2 , LiAlH_4 , NH_3 , formic acid or as carbohydrates, on carbon materials (graphenes) and on imidazolium-based ionic liquids.

- Carbon is widely distributed in nature. The three natural isotopes of carbon are ^{12}C , ^{13}C and ^{14}C . ^{13}C finds its use in isotopic studies. ^{14}C being radioactive is used in the determination of the age of objects by radiocarbon dating.
- The various allotropic forms of carbon are diamond, graphite, fullerene (crystalline) and coke, coal, charcoal, lamp black (amorphous).
- The carbon atom in graphite is sp^2 hybridised and has a planar, layered structure. The layers slip over each other and hence it is used as a lubricant, and is a good conductor of electricity.
- Diamond is sp^3 hybridised and strongly bonded with the neighboring atoms being situated at the corners of a regular tetrahedron. It is the hardest substance known.
- Fullerene is soccer ball-shaped with pentagon and hexagons in its structure.
- Coke, coal and charcoal are the amorphous forms of carbon.

Review Questions

1. Discuss the anomalous position of hydrogen in the periodic table. Explain the various methods of preparation of hydrogen.
2. Write down the various industrial methods of the manufacture of hydrogen.
3. Explain in detail the different types of hydrides.
4. Storage and transportation of hydrogen is a challenging task! Explain the various techniques employed for the safe storage of hydrogen.
5. On the basis of their structure and bonding explain the various allotropes of carbon.
6. Discuss in detail the applications of carbon and hydrogen.

Multiple Choice Questions

1. Which of the following is not an isotope of hydrogen
 (a) ^1H (b) ^2H
 (c) ^3H (d) ^4H
2. Which of the following methods is not used for the manufacture of hydrogen gas
 (a) Steam reforming (b) Action of acids on metals
 (c) Passing steam over red-hot coke (d) Electrolysis
3. In the steam reforming process hydrocarbons are mixed with steam and passed over _____ catalyst at $800 - 900^\circ\text{C}$.
 (a) Nickel (b) Fe_2O_3
 (c) Cr_2O_3 (d) TiO_2

4. Hydrogen can be stored as
 - (a) Hydrides
 - (b) Inside carbon nanotubes and carbon bucky balls
 - (c) Carbohydrates
 - (d) All the above
5. Which of the following is an ionic hydride
 - (a) CsH
 - (b) NH_3
 - (c) SiH_4
 - (d) PH_3
6. The hydrides with non-stoichiometric composition are
 - (a) Covalent hydrides
 - (b) Metallic hydrides
 - (c) Ionic hydrides
 - (d) Polymeric hydrides.
7. Hydrides in which hydrogen is adsorbed and retained in the interstices of the metal are
 - (a) Polymeric hydrides
 - (b) Ionic hydrides
 - (c) Metallic hydrides
 - (d) Covalent hydrides.
8. The isotope of carbon used in spectroscopic and chemical studies is
 - (a) ^{11}C
 - (b) ^{12}C
 - (c) ^{13}C
 - (d) ^{14}C
9. Which of the following isotope of carbon is radioactive
 - (a) ^{11}C
 - (b) ^{12}C
 - (c) ^{13}C
 - (d) ^{14}C
10. The allotrope of carbon with a layered structure is
 - (a) Graphite
 - (b) Diamond
 - (c) Fullerene
 - (d) Coke
11. The carbon atom of diamond is
 - (a) sp^2 hybridised
 - (b) sp hybridised
 - (c) sp^3 hybridised
 - (d) None of the above
12. Which of the following is not an amorphous form of carbon
 - (a) Diamond
 - (b) Coke
 - (c) Coal
 - (d) Charcoal

Solution

- | | | | | | | | |
|-------|--------|--------|--------|-------|-------|-------|-------|
| 1 (d) | 2 (b) | 3 (a) | 4 (d) | 5 (a) | 6 (b) | 7 (c) | 8 (c) |
| 9 (d) | 10 (a) | 11 (c) | 12 (a) | | | | |

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